Fate of Bromate Formation in Water Treated by Ozone-based Advanced Oxidation Processes

BY

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DEDICATION

This work is dedicated to the memory of my late Father; Alhaji Zubair A. Banu.

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All praises are due to Allah (SWT) for giving me the courage to pursue this research and the overall completion of my studies in good health. This work would not have been possible without the help and support of a number of people and institutions through time. I am glad to have the chance to recognize them here.

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THESIS ABSTRACT

Name: Abdulrazaq Zubair

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Water is considered as scarce resources in the Kingdom of Saudi Arabia, like many other gulf countries, due to the low annual rainfall rates and limited fresh renewable groundwater resources. It is therefore imperative to keep these limited resources free of contaminants and the by-products of their remediation.

Bromate formation during the oxidative treatment of bromide-containing water has been of great concern ever since bromate was classified as a potential carcinogen. Saudi Arabian groundwater is coincidentally high in bromide content, and the potential of forming bromate during the treatment of such water is high.

This study investigated the extent of bromate formation under different treatment conditions of Ozone-based AOP. The effects of pH adjustment and Ammonia addition in controlling bromate formation were also investigated. Several parameters were studied for the AOP treatment conditions and Bromate control.

The results of this study showed that Continuous Ozonation (1 liter per minute) is the most effective ozone-based AOP technique for complete degradation of phenol in Saudi Arabian water within five minutes. A pH level of 6.0 and an ammonia dosage of 1.5 ppm of were found to be the optimum treatment conditions needed to prevent bromate formation in Saudi Arabian water.

ملخص الرساله

الاسم: عبد الرزاق زبير

عنوان الرساله: مصير البروميت المتكون فى المياه المعالجه من عمليات الاكسده المتقدمه بواسطه غاز الاوزون.

التخصص: علوم البيئه.

التاريخ: يونيو 2009

تقيّم المياه في المملكة العربية السعودية على أنها ذات مصادر قليلة مثلها مثل باقي دول الخليج العربي نظرا لقلة معدل هطول الأمطار ونظرا لقلة مصادر المياه الجوفية العذبة المتجددة . لهذا السبب فمن الأهمية بمكان أن تحفظ هذه المصادر المحدودة بعيدا عن أي ملوثات.

المياه التي تحتوي على البروميد وأثناء عملية الأكسدة والمعالجة تجرى باهتمام وحيطة بالغة نظرا لأن البروميد مصنف كمادة مسرطنة ومن المصادفة أن المياه الجوفية في المملكة تحتوي على نسب عالية من البروميد وامكانيه تكوين البروميد خلال المعالجه تكون عاليه.

بحث الدراسة مدى تأثر المياه الملوثة بالبروميد بالمعالجة بالأوزون تحت ظروف مختلفة ، تأثير التحكم بالحمضية والقلوية ، إضافة النشادر.عدة عوامل درست للأكسدة الحديثة بالأوزون وتحت شروط معينة وتحكم بنسبة البروميد.

نتائج هذه الدراسه اثبتت ان التدفق المستمر للاوزون بمعدل 1 لتر في الدقيقه هو اكثر الطرق تاثيرا للمعالجه الكامله للفينول في الماء خلال خمسه دقائق. وجد ان مستوي حمضه 6 و 1,5 جزء من المليون من الامونيا هي الظروف الامثل لمنع تكون البروميد في المياه الجوفيه في المملكه.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The 21st century mankind has to face the problem of water as an important threat. According to the World Health Organization (E. Koch et al., 1993), the shortage or even lack of water affects more than 40% of the world population due to political, economical and climatological reasons. Besides, more than 25% of the world population suffers from health and hygienic problems related to water. Despite the plans carried out by United Nations Organization in recent years, 110 million people still have no access to improved water supply and sanitation, especially concentrated in underdeveloped countries of Africa, Asia and Latin America (WHO, 2000).

On the other hand, the production and storage of oil derived fuels and other industrial activities, have led to a wide spread of many contaminants into the environment. The contamination is particularly relevant for groundwater because of accidental release from underground storage tanks and pipelines in petrochemical sites. This fact, together with the need to restore this water for consumption purposes, makes

practically essential the purification of groundwater to achieve the desired degree of quality.

Because of an increasing social and political concern on environment, the research field of water purification has been extensively growing in the last decades as regulations against hazardous pollutants have become stricter in many countries. More recently, reflecting a new environmental conscience, the European Directive 2000/60/CE (European Commission, 2000) stressed the need to adopt measures against water pollution in order to achieve a progressive reduction of pollutants.

The drinking water industry, over the last decades has relied on the use of Advanced Oxidation Processes (AOP) as promising treatment techniques for the removal of contaminants in water. These technologies have been recognized as effective water treatment methods not only for the degradation of organic molecules, but taste and odour control in water as well. They are also found to be very active against a wide range of micro-organisms including more effective treatment of *Cryptosporidium* oocysts and *Giardia* in waste and drinking water (Bull and Cottruvo, 2006). The most notable limitation of this technology however, is the formation of bromate as a major by-product in the AOP treatment of water with high bromide content. The level of bromate formed during ozonation is dependent on the amount of bromide found in the source water, the dosage of ozone and the pH of the water among other factors (Song et al., 1996). Bromate management is therefore important when Advanced Oxidation Processes are used for drinking water processes.

1.2 ADVANCED OXIDATION PROCESSES (AOP)

The term AOP describes all oxidation processes which are characterized by the formation of a common chemical: **hydroxyl radicals ($OH^{\bullet}$).** These radicals are extremely reactive and capable of oxidizing some of the organic contaminants in water. AOP first appeared in the literature in 1988. Since the first work with Ozone/UV, several methods have been developed and studied. It is now been divided into two main groups, namely; UV/Oxidation processes and the Non-UV processes. The UV/Oxidation processes e.g. UV/H_2O_2, UV/O_3, UV/H_2O_2/O etc are the most commonly used. They are destruction processes that oxidize organic contaminants such as MTBE, phenol, styrene, Atrazine, xylene, benzene, toluene etc in water by addition of strong oxidizers and irradiation with UV light. The oxidation reactions are achieved through the synergistic action of high intensity UV light in combination with ozone and/or hydrogen peroxide in a patented treatment reactor. Through direct photolysis, the UV light reacts with the oxidant (H_2O_2 or O_3) to generate hydroxyl radicals **($OH^{\bullet}$)**, which are highly reactive, and are second only to fluorine in relative oxidation potential. The generation of **($OH^{\bullet}$)** from ozone and hydrogen peroxide can be shown as thus;

$$\mathbf{H_2O_2 + hv\ (200\text{-}300nm) \rightarrow 2OH\bullet} \qquad \mathbf{(1)}$$

$$\mathbf{O_3 + H_2O + hv\ (420\text{-}600nm) \rightarrow 2OH\bullet} \qquad \mathbf{(2)}$$

The hydroxyl radicals then attack the organic molecules resulting in the destruction of the parent organic compound. The reaction is aided by the direct photolysis of the

organic molecule by the UV light, which can break or activate certain atomic bonds making the molecule more susceptible to oxidation. With sufficient oxidation and exposure to UV energy, the reaction by-products are carbon dioxide, water, and the appropriate inorganic salt (if complete oxidation is achieved).

There are several AOPs studied for water treatment with different contaminants, such as: UV/Fenton and dark-Fenton's reactions for MTBE, (Yeh and Novak, 1995; Charton *et al.,* 1997, Ray et al., 2002), O_3/H_2O_2 MTBE, BTEX, Phenol and DCE (Safarzadeh-Amiri, 2001), UV/H_2O_2 process for MTBE, Phenol, Atrazine and EDC (Wagler and Malley, 1994; Stefan *et al.,* 2000; Cater et al., 2000b), O_3/UV process, O_3/H_2O_2 process for MTBE, Benzene etc (Von Gunten and Junan Carlo, 2001), sonolytic (Kang and Hoffmann, 1998), Photocatalytic oxidation of MTBE (Barreto *et al,*. 1995), and O_3/H_2O_2/UV process for MTBE degradation (Tawabini et al, 2007, 2008).

1.2.1 Ozone-Based Advanced Oxidation Processes

All AOP processes that involve the use of Ozone are collectively called **"Ozone-based AOP techniques"** e.g. O_3/UV, O_3/H_2O_2, $O_3/UV/H_2O_2$ etc. There has been an increasing interest in the last decades in using ozone to treat effluents containing hazardous pollutants with the development of large-scale ozone generators along with reduced installation and operating costs (Marc Pera-Titus et al., 2003) compared to

other oxidizing reagents, ozonated water is more efficient in pollutant degradation and it is not harmful for most of the organisms, because no strange compounds are added to treated waters. Ozonation has been widely used for drinking water treatment, bacterial sterilization, odor, algae, and trihalomethane removal and organic compound degradation (K.I. Abe et al., 1996) but its application to water treatment is limited due to its high energy demand. Thanks to its oxidizing power, ozone is a potential pre-treatment agent to transform refractory compounds into substances that can be further removed by conventional methods (Von Gunten et al., 2004). Thus, the ozonation of dissolved compounds in water can constitute an AOP by itself, as hydroxyl radicals can be generated from the decomposition of ozone, which might be catalyzed by hydroxyl ions or initiated by the presence of traces of other substances, like transition metal cations (Hoigne et al., 1985). As pH increases, so does the rate of decomposition of ozone in water.

Ozone (O_3) was first used to disinfect drinking water in a large-scale application during the 1890s. Ozone is a strong oxidant, but is relatively selective, is slightly soluble in water, and its water solution is moderately stable. Although ozone has a highly favorable redox potential, targeted organic compounds have the tendency to react very slowly with ozone, because chemical oxidation processes are limited by chemical kinetics despite the fact that all organic compounds are thermodynamically unstable in respect to chemical oxidation (Glaze, 1989). Recently researchers have shown that enhancing ozone conversion to reactive free radicals (i.e. hydroxyl

radicals) can eliminate rate limitations (Von Gunten et al., 2004). This may be achieved by adding H_2O_2 and/or UV irradiation. Ozone-based processes form hydroxyl radicals via a sequence of reactions that is initiated when ozone is decomposed by the hydroxide ions. The first type of those enhanced processes (O_3/H_2O_2) is commercialized under the name Perozone. Because of its simplicity and ease of operation, this process has been promoted as the most practical of the AOPs.

When O_3 is added to water, it participates in a complex chain of reactions that result in the formation of radicals such as the hydroxyl radical ($OH^{\cdot}$) and the superoxide radical ($O_2^{\cdot-}$) (Hoigné., 1998). Like O_3, these radical products ($OH^{\cdot}$ and $O_2^{\cdot-}$) are oxidants that are capable of contaminants destruction. Of the radical intermediates formed in ozonated water, $OH^{\cdot}$ is the most powerful oxidant, even more powerful than O_3 itself. Oxidation of ethers by O_3 is known to occur very slowly with second-order kinetic rate constants less than 1 $M^{-1}s^{-1}$ (Buxton et al., 1988). By contrast, oxidation of ethers by radical oxidants is extremely rapid. Hydroxyl radicals react with Phenol according to a rate constant of 1.6×10^9 $M^{-1}s^{-1}$ (Buxton et al., 1988). In an O_3/H_2O_2 system, H_2O_2 is used in conjunction with O_3 to enhance the formation of hydroxyl radicals. Since O_3 decomposes rapidly, it is typically produced on-site using a generator fed with dried compressed air or oxygen (Hoigné, 1998). The gas mixtures produced from air and oxygen by an ozone generator usually consist of 0.5 to 1.5% and 1 to 2% by volume O_3, respectively (Montgomery, 1985). The use of air to generate ozone requires dehumidification, which may be cost prohibitive relative to the use of pure liquid oxygen. In addition, larger quantities of ozone can be produced

from a unit of liquid oxygen (14% O_2 by weight) compared to a unit of compressed air (2% O_2 by weight), which facilitates greater mass transfer of the ozone into the source water. Finally, ozone can be generated from liquid oxygen using less energy than it can be from compressed air.

Another method of ozone-based AOP is the combination of O_3/UV or O_3/UV/H_2O_2. Photolytic ozonation (O_3/UV process) is an effective method for the oxidation and destruction of toxic and refractory organics in water ((Von Gunten and Junan Carlo, 2001) and has a significant potential as a water treatment process. Basically, aqueous systems saturated with ozone are irradiated with UV light of at least 253.7 nm. The extinction coefficient of ozone at 253.7 nm is 3300M^{-1} cm^{-1}, much higher than that of hydrogen peroxide. The decay rate of ozone is around 1000 times higher than that of hydrogen peroxide (Glaze et al., 1991). It was shown that photolytic ozonation is more effective for the destruction of some organic compounds than either UV-photolysis or ozonation alone. However, some researchers (Smith et al., 1990) have found photolytic ozonation to be only more effective than ozonation alone in some cases.

1.2.2 Pathways for Ozone-based AOP

One of the most important facts to mention when studying the oxidation of organic contaminants by ozone is the high influence of the pH in the kinetics and pathways of

the reaction. This arises from the fact that pH affects the double action of ozone on the organic matter, that may be a *direct* or an *indirect* (free radical) ozonation pathway (Song et al., 1996). These different reaction pathways lead to different oxidation products and are controlled by different kinetic models. At low pH, ozone exclusively reacts with compounds with specific functional groups through selective reactions such as electrophilic, nucleophilic or dipolar addition reactions (i.e. direct pathway) (Song et al., 1996). On the other hand, at basic conditions, ozone decomposes yielding hydroxyl radicals, which are high oxidizing species that react in a non-selectively way with a wide range of organic and inorganic compounds in water (i.e. indirect ozonation) (Buxton et al., 1988). Normally, under acidic conditions (pH <4) the direct ozonation dominates, in the range of pH 4–9 both are present, and above pH >9 the indirect pathway prevails.

1.3 WHAT IS BROMATE?

Bromate (BrO_3^-) is an oxyanion of bromine which can be found in potable drinking water. It is a by-product mostly generated when raw water sources (both surface and ground waters) containing bromide ions are treated with ozone. It is also formed in water following pretreatment processes including hypochlorination, where it is a contaminant of hypochlorite feedstocks.

Bromate formation has been the major barrier in the use of ozone for water treatment where the source water contains bromide, particularly given the challenging targets

set for the maximum allowable bromate concentration. A number of bromate modeling tools have been developed for predicting bromate formation in order to provide a better understanding of when bromate regulations may be exceeded at Water Treatment Works (Magazinovic et al, 2004)). The ultimate goal of such models is to provide a bromate formation tool capable of accurately controlling bromate formation by changing operational conditions during ozonation to bring bromate formation below the maximum allowable concentration.

1.4 HEALTH EFFECTS OF BROMATE

While bromide ion is mostly not considered to be harmful in the concentrations found in drinking water, bromate pose serious health concerns. Information on the toxicity of bromate comes from accidental or intentional poisonings in people and from studies on laboratory animals.

Some people who ingested large amounts of bromate had gastrointestinal symptoms such as nausea, vomiting, diarrhea and abdominal pain. Some individuals who ingested high concentrations of bromate also experienced kidney effects, varying degrees of central nervous system depression, hearing loss, haemolytic anaemia and pulmonary oedema (USEPA, 1998). Most of these effects are reversible. Irreversible effects include renal failure and deafness, both of which have been observed following the ingestion of 240–500 mg of potassium bromate per kg of body weight (185–385 mg of bromate per kg of body weight) (USEPA, 1999b). However, these

people were exposed to bromate levels many thousands of times the amount that would come from drinking water at its standard (10 μg/L) (EU, 1998).

In terms of reproductive effects, some people may be at greater risk for developing reproductive problems from bromate exposure or have concerns for their pregnancy or nursing infant due to some scientific evidence which shows that bromate alters the gene (mutagenic agent) (USEPA, 1999b). The information on the effects of bromate on reproductive health is limited, but does not indicate a concern at levels near the drinking water standard. Because bromate can cause health effects in kidneys, it is possible that those with pre-existing kidney conditions could be at greater risk. No epidemiological studies were located on non-carcinogenic or carcinogenic effects of bromate exposure in humans (WHO, 1994).

Long-term exposure to high levels of bromate has also caused cancer in laboratory animals. Whether bromate can cause cancer in people is not certain, but the World Health Organization (WHO, 1993) and the International Agency for Research on Cancer (IARC) classified Bromate as group 2B or a 'potential human' carcinogen (WHO, 1993). It was due these facts that the control and regulation of bromate in drinking water became essential.

1.5 BROMATE REGULATORY UPDATE

Bromate contamination of potable supplies has been an issue since the mid 1980s, when animal studies suggested a link between low-level long term exposure and tumour formation. This prompted the World Health Organization (WHO) to classify bromate as a potential human carcinogen leading to implementation of 25 µg/L of bromate in drinking water in the late 1980's. This limit was mainly due to limitations in bromate analysis, which was effectively restricted to use of relatively crude titrimetric methods. Advanced techniques have been developed to analyze bromate at and below the regulatory limits, with Ion Chromatography (IC), coupled with conductivity detection (IC-CD), post column reaction and Ultraviolet (UV) detection (IC-PCR), or Inductively Coupled Plasma-Mass Spectrometry (IC-ICPMS). The World Health Organization (WHO), European Union (EU), and United States Environmental Protection Agency (USEPA) have set a new low drinking water standard of 10µg/L (EU, 1998; USEPA 1998). They also classify bromate as the only ozonation by-product regulated in drinking water.

In addition, the USEPA in its stage 1 Disinfectants and Disinfection by-products Rule has recommended a maximum contaminant level goal (MCLG) of zero for bromate. The concentration of bromate found in water disinfected with ozone range from less than 1 ppb to over 150 ppb (Von Gunten *et.al*, 1996).

1.6 RESEARCH SIGNIFICANCE

Many contaminants have found their ways into the surface and groundwater system due to discharges from the industries, workshops, laboratories and treatment plants. Prominent among these contaminants are PHCs, Dioxins, PCBs, MTBE, Phenol, BTEX, etc.

Over the last decades, AOPs have emerged as promising treatment techniques for the removal of these contaminants in water. They have been recognized as effective water treatment methods for complete degradation of organic contaminants in water. One of the limitations of these techniques however, is the formation of bromate formed during the oxidative treatment of bromide-containing water via ozonation. Saudi Arabian groundwater is known to have extremely high bromide content (5 ppm), (Tawabini et al., 2007) coupled with the high vulnerability of contamination from oil wells, pipelines and petrochemical industries.

The world health organization (WHO) and the International Agency for Research on Cancer (IARC) classified Bromate as a potential human carcinogen. Bromate poisoning also cause abdominal pains, hearing impairment, kidney failure and at high doses, may cause death. It is the only disinfection by-product (DBP) that is regulated in drinking water. As such, the USEPA and EU have set a maximum limit of 10 ppb for this contaminant in drinking water. In addition, the USEPA recommends a maximum contaminant level goal (MCLG) of zero for bromate (USEPA, 1998). Recently, Saudi Arabian Standards Organization (SASO) recently set a new drinking

water standard regulation related to bromate concentration which was lowered from 25 ppb to 10 ppb (Standard No. 409/2000).

Based on the aforementioned, it became necessary to find an appropriate method to minimize and if possible, completely prevent bromate formation as a by-product of the ozone-based AOPs. To this end, no work has been done to assess the extent of bromate minimization during the ozonation of contaminated Saudi Arabian water. Even on a global scale, only very few publications are available on the simultaneous degradation of contaminants with AOP techniques in combination with bromate reduction methods

1.7 PROJECT APPROACH

The approach to the execution of the project was through conducting several ozone-based AOP experiments in a bench scale reactor using phenol as the target contaminant and phenol simulated (synthetic) water as the primary material under different treatment conditions with strategies to minimize bromate formation.

- The AOP treatment conditions for the removal of phenol were: ozone dosage, UV intensity and contact time.

- The bromate reduction procedure include: changing the pH levels and addition of different concentrations of ammonia.

The reduction in phenol concentrations as well as formation of bromate ions in the treated water were observed over a period of 30 minutes at specific intervals (0, 0.17, 5, 10, 20 and 30 minutes respectively). The concentrations of the residual phenol were analyzed using High Performance Liquid Chromatography (HPLC), while Ion Chromatography (IC) was used to for bromate analysis. Finally, an appropriate ozone-based AOP technique for the removal of phenol within the shortest time was identified, while the optimum conditions (pH and Ammonia level) for the prevention of bromate formation were also identified.

CHAPTER 2

LITERATURE REVIEW

Since the classification of Bromate as a potential human carcinogen, a lot of studies have been done to elucidate appropriate techniques to minimize and control its formation during the ozonation of bromide-containing water. Efficiency of these techniques have been compared in many publications, factors affecting bromate formation have been extensively investigated, modeling efforts for it have been performed, its toxic effects have been discovered, and many studies have been carried out and are still going on to ascertain the most reliable method of controlling its formation with the aim of producing drinking water containing the minimum possible concentration of bromate that is safe for human consumption.

2.1 PHENOL DEGRADATION BY OZONE-BASED AOP

The need to restore phenol contaminated sites to avoid further risks to the environment has aroused in the last few years, the development of effective methods for phenol removal. The main goal is to achieve a complete mineralization to CO_2

and H_2O in addition to smaller amounts of some ions or at least to produce less harmful intermediates. The conventional pollutant destructive technologies include biological, thermal and chemical treatments (Jardim et al; 1997). The former usually require a long residence time for microorganisms to degrade the pollutant, because they are affected by Phenol's toxicity; thermal treatments present considerable emission of other hazardous compounds; and the latter, which include processes as flocculation, precipitation, adsorption on granular activated carbon (GAC), air stripping or reverse osmosis (RO), require a post-treatment to remove the pollutant from the newly contaminated environment (Danis et al; 1998).

Alternative methods to these well-established techniques involve the oxidation of Phenol with reagents such as air or oxygen in wet oxidation and supercritical wet oxidation (Lee et al; 2002, Li et al; 1991, Lin et al; 1998), electrons in electrochemical oxidation (Huang et al; 1992, Comminelis; 1994, Rodgers et al; 1999), potassium permanganate, chlorine, hydrogen peroxide and ozone (Chamarro et al; 1996, Yin et al; 1999). Among these techniques, the so-called "Advanced Oxidation Processes" (AOPs) (Glaze et al; 1987, Glaze et al; 1994) appear to be a promising field of study, which have been reported to be effective for the near ambient degradation of soluble organic contaminants from waters and soils, because they can provide an almost total degradation (Ben´ıtez et al; 1995, 1997, Casero et al, 1997).

In their work titled "Removal of phenol from water using ozone", Kadir and Uzman (2008), demonstrated how continuous ozonation (ozone only) at the rates of 2, 4 and

6 g/Lh can be used to degrade phenol completely after 40 minutes (100% removal) using 25, 50, 75 and 100 mg/L of phenol in a series of experiments carried out in a batch reactor. They showed that in the reaction of ozone with phenol, in addition to catechol (C) and hydroquinone (HQ), p-benzoquinone (PBQ) and o-benzoquinone (OBQ) are the likely primary oxidation products. The others are more oxidized species, and CO_2 and water the final oxidation products. The detected degradation products are shown in Fig. 2.1 below. This initial attack of the ozone molecule leads first to the formation of ortho- and para-hydroxylated by-products. These hydroxylated compounds are highly susceptible to further ozonation. The compounds lead to the formation of quinoid and, due to the opening of the aromatic cycle, to the formation of aliphatic products with carbonyl and carboxyl functions.

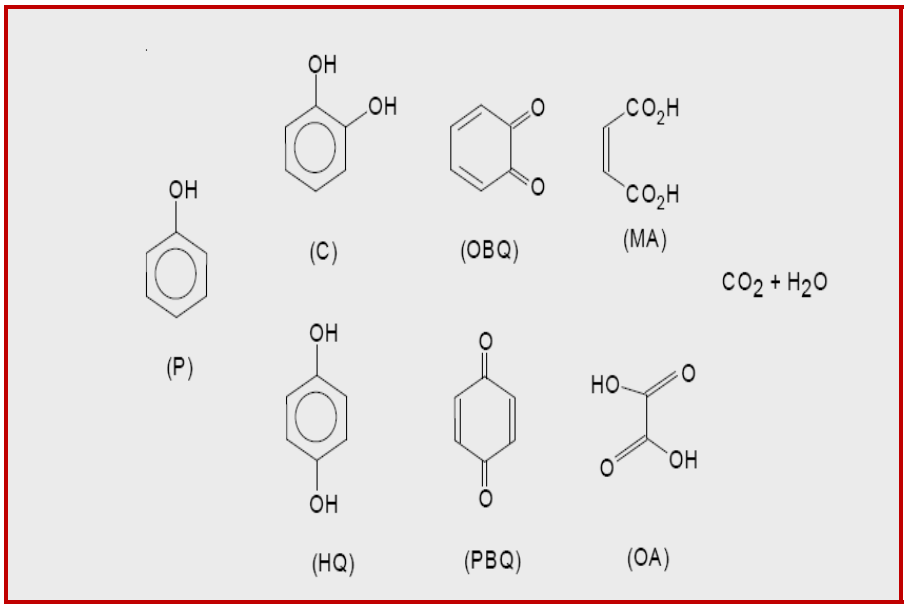

Figure 2.1: Reaction pathway in the degradation of phenol.

Spark et al (2000) utilized ozone/hydrogen peroxide to degrade phenol in water at different pH conditions, while Rahmani et al., (2006) investigated the photocatalytic degradation of phenol by UV/TiO_2. Marc Pera-Titus et al., (2004) did a comprehensive general review on the degradation of chlorophenols by means of AOP. They recommended the ozone-based AOP as the most promising and cost-intensive technology for the treatment of waters (waste, ground and surface waters) containing not only by phenol, but other non-easily removable organic compounds.

2.2 FACTORS INFLUENCING BROMATE FORMATION

The formation of bromate during ozonation is strongly dependent on the characteristics of the water to be treated and the amount of ozone contacting the water. The following are important variables for bromate formation:

1. **Bromide concentration**: Given that bromide is oxidized by ozone to bromate, an increase in bromide inevitably leads to an increase in bromate for a constant ozone dose and contact time (Legube et al., 2004). Conversion of bromide to bromate is usually between 10–50% during ozonation (Song et al., 1996). Typical concentrations of bromide in natural waters usually range from 30–200 mg/L, with an average of 100 mg/L (Amy et al., 1994), however this can be greater than 500 mg/L (Legube et al., 2004). Amy et al. (1994) have suggested that up to 30 mg/L of bromate can form from an average bromide concentration of 100 mg/L—significantly above the target bromate

concentration of 10 mg/L. This equates to a 20.5% conversion rate of bromide to bromate in terms of Br. Groundwater sources can have particularly high bromide concentrations due to ingress by salt water, road run-off following the salting of roads in winter and also as a result of dissolution from sedimentary rocks (Magazinovic et al., 2004; Butler et al., 2005).

2. **pH:** As the ozonation pH of the water is increased, the rate of bromate formation increases (Pinkernell andvon Gunten, 2001). In part, this is as a result of the formation of the more unstable and reactive BrO^- compound at high pH as the equilibrium between $HBrO \leftrightarrow Br^- + H^+$ shifts to the right as the concentration of hydrogen ions decreases. In addition, hydroxyl radical formation is promoted at high pH due to the increased concentration of hydroxyl ions present and the lower stability of ozone at high pH (Song et al., 1997; Siddiqui et al., 1998). Bromate formation has been shown to increase from 10 mg/L at pH 6.5 to 50 mg/L at pH 8.2 (Legube et al., 2004) whilst Krasner et al. (1994) observed a 60% decrease in bromate formation for each drop in pH unit. The ozonation pH is widely regarded as being the most effective bromate control strategy at WTW and should be considered the best available treatment for bromate control (Ozekin and Amy, 1997). However, this must be balanced by the increased formation of brominated organic compounds as pH is reduced (USEPA, 1999a). Additionally, the cost of pH reduction may be prohibitive for high alkalinity waters due to the volume of acid required (von Gunten, 2003b).

3. **Applied ozone concentration and contact time**: An important consideration in the conversion of bromide to bromate is the specific goal of the remediation (von Gunten et al., 2001). According to Diamadopoulus et al., (2004), Contact Time is the product of the time of exposure (min.) and the residual disinfectant concentration of ozone measures at the end of the water treatment, i.e. ozone dose x contact time. The efficiency of any disinfection or remediation may be characterized by the 'Ct' factor (USEPA, 1999b). The relationship between bromate formation and Ct follows a linear function with an increase in Ct leading to an increase in bromate formation (von Gunten and Hoigne, 1996; Legube et al., 2004; Diamadopoulus et al., 2004). Bromate formation increases as the contact time (Ct) increases under the same ozone dose. Increasing ozone dose while keeping a constant contact time (Ct) resulted in increased bromate formation (Diamadopoulus et al., 2004).

4. **DOC concentration**: Both the concentration and nature of organic material in water can affect bromate formation. During ozonation, any natural organic matter (NOM) present in the water generally reduces bromate formation. This is because ozone and hydroxyl radicals are consumed by the oxidation of organic molecules and therefore taken away from the bromate formation pathways. However, this is not always the case because if a residual ozone concentration is required for disinfection, more ozone may need to be added resulting in similar or in some cases increased concentrations of bromate. The presence of NOM and bromide during ozonation can also lead to the

formation of brominated organics. The exact identity of all of these brominated compounds has yet to have been fully established (and are not currently regulated for), but they are believed to be a higher risk to health than chlorine-based DBPs (Song et al., 1997). From a bromate modeling point of view, the presence of NOM can be the principal stumbling block in producing accurate bromate formation models due to the complexity and site-specific nature of NOM and its complex interactions with ozone (Westerhoff et al., 1998; Sohn et al., 2004). This prevents a full and accurate understanding of the reactions between ozone and NOM.

5. **Alkalinity:** The presence of inorganic carbon species increases bromate formation because both carbonate (CO_3^{-2}) and bicarbonate (HCO_3^-) species can form the carbonate radical (CO_3^-) as a result of oxidation by hydroxyl radicals (von Gunten, 2003a). Once the carbonate radical has been formed, this can convert hypobromite into the hypobromite radical (BrO^-) and then bromate (Kim et al., 2004).

6. **Ammonia concentration**: The presence of ammonia in water acts as a scavenger of hypobromous acid (HOBr) during ozonation, an important intermediate in the formation pathway of bromate (Pinkernell and von Gunten, 2001; von Gunten, 2003a). HOBr reacts with ammonia to form bromamine compounds, which, in turn, can be converted back to bromide through oxidation by ozone. Ammonia can therefore remove a significant intermediary from the bromate formation path and reduce the amount of

bromate formed (Song et al., 1997). Ammonia may be present naturally in waters to be ozonated, or alternatively can be added prior to ozonation as a bromate prevention strategy. The addition of a high concentration of ammonia (1.5 mg/L) has been shown to reduce bromate formation by around 5 mg/L when applied to water containing 100mg/L Br^- under constant conditions (Ozekin and Amy, 1997). This reduction, although small, may be critical for those WTW where bromate levels are around the maximum permitted concentration. However, this must be tempered by the fact that above a certain concentration, the addition of ammonia has no further effect on bromate reduction. Therefore, for waters that contain naturally high to medium concentrations of ammonia, the addition of further ammonia may offer no further benefit (von Gunten, 2003b). Furthermore, any un-removed ammonia may act as a nutrient for nitrifying bacteria once in distribution (USEPA, 1999a). An additional strategy for bromate control using ammonia is the combined pre-chlorination/ammonia addition before ozonation. This has been shown to reduce bromate formation in lake Zurich water from 10 mg/L to 2 mg/L (conditions: Cl_2 0.7 mg/L; NH_3 400 mg/L; 1.5 mg/L O_3; Br^- 90 mg/L) and may be a promising control strategy involving lower ammonia addition to drinking water (Buffle et al., 2004).

7. **Temperature:** Increased temperature has been shown to increase the rate of bromate formation as a result of increased reaction kinetics and because the equilibrium between $HBrO \leftrightarrow BrO^- + H^+$ shifts to the right as the

temperature increases due to a commensurate increase in the acidity constant (Legube et al., 2004). The effect of temperature has been shown to be more pronounced at higher ozone doses. For example, Galey et al. (2004) observed that at an ozone dose of 1 mg/L the bromate formation was 8 mg/L at both 5 and 24^{o}C while at 2.5mg/L the bromate formation was 22 mg/L at 5^{o}C and 37cmg/L at 24^{o}C. Water temperature is therefore one of the important factors that determines bromate formation.

2.3 BROMATE FORMATION MECHANISM

Ozone's ability to oxidize bromide to bromate (BrO_3^-) has been known and studied as far back as 1942. However, detailed mechanistic and kinetics investigations were only initiated in the 1980's following the WHO reports that classified bromate as a potential carcinogen. The number of publications on Bromate formation increased significantly in the 1990's. Since then, complex pathways of bromate formation during ozonation has been elucidated satisfactorily. Bromate is formed by ozonation/oxidation of bromide-containing water. Bromide ions (Br^-) enter natural waters as a result of natural processes (salt water intrusion, geologic sources) and anthropogenic activities (potassium mining, coal mining, agricultural sources etc). Bromate formation occurs via both direct ozonation (molecular ozone) and indirect (radical) oxidation pathways. Song (1996) gave a simplified version of bromate formation pathways.

Direct/Indirect:

$$Br \xrightarrow{O_3} HOBr/OBr \xrightarrow{OH^-} OBr \xrightarrow{Disproportionation} BrO_2^- \xrightarrow{O_3} BrO_3^- \quad (3)$$

Indirect/ Direct:

$$Br^- \xrightarrow{OH^-} Br \xrightarrow{O_3} OBr \xrightarrow{Disproportionation} BrO_2^- \xrightarrow{O_3} BrO_3^- \quad (4)$$

Direct:

$$Br^- \xrightarrow{O_3} HOBr/OBr^- \xrightarrow{O_3} BrO_2^- \xrightarrow{O_3} BrO_3^- \quad (5)$$

Hypobromous acid (HOBr) and hypobromite (OBr^-) are the intermediate products leading to the formation of bromate. The reaction rates of pathways involving O_3/BrO^- is higher than that of O_3/HOBr. Thus, bromate formation under basic conditions is higher than that expected in acidic medium (Von Gunten and Hoigne, 1992; Song 1996; Minear and Amy, 1996). Increasing the pH causes more rapid ozone decomposition resulting in more $OH^{\bullet}$ radical generation, and thus increased bromate formation (Yates and Stensrom, 1993; Westerhoff et al., 1998).

2.4 BROMATE MINIMIZATION STRATEGIES

As a result of USEPA and EU setting bromate drinking water standard at 10µg/L, control strategies to minimize bromate formation have become necessary. A lot of publications are available concerning different bromate reduction methods during

ozonation. Powdered activated carbon (PAC) and granular activated carbon (GAC) adsorption, biofiltration and biological reduction were applied for bromate removal. According to Kirisits (1999), batch experiments have indicated that bromate reduction in GAC occurs mainly due to biological activity, not abiotic processes. Salt and dissolved organic carbon dramatically inhibits bromate reduction. Activated carbon processes may not be economical for bromate reduction (Minear and Amy, 1996). Bromate removal via UV photolysis and photocatalysis were also studied in many publications and it has been reported that these methods are not practical for bromate reduction due to the long reaction time required (Mills *et al*., 1996; Noguchi *et al.,* 2003). Ferrous ion (Fe^{2+}) coagulation after ozonation is one of the efficient bromate reduction method but the required Fe^{2+} concentration is very high even at very low bromate concentrations (Siddique *et al.,* 1994).

Based on kinetic understanding of bromate formation, two main bromate control strategies have been recommended by many scientists and applied to drinking water ozonation: **Ammonia addition and pH suppression**. Bromate forms through three major pathways (as shown in equations 3, 4 and 5). Two of the pathways require free bromine ($HOBr/OBr^-$) as an intermediate. Ammonia reacts with free bromine to form bromoamines, which do not participate in bromate formation (Hofmann, 2000); ammonia therefore can relatively block these two pathways. The third pathway (indirect/direct (I-D) pathway) does not require free bromine and is not significantly affected; ammonia may therefore reduce bromate formation but will not but will not completely eliminate it. The effect of Ammonia however, is insignificant at higher pH

values due to the fast O_3/BrO^- reaction (Hofmann and Andrews, 2006). They also reported that bi-carbonate alkalinity in the presence of ammonia would inhibit bromate formation since the third pathway that ammonia does not block requires hydroxyl radicals. Further, ammonia is a naturally occurring compound; so many waters may therefore have an inherent resistance to bromate formation.

The Ontario Ministry of the Environment Drinking Water Surveillance Program database of 142 treatment facilities showed average ammonia concentrations ranging from 3 to 475 µg/L as N, with an overall average of 50 µg/L for the period of 1990–1998 (OMOE; 1999). An ammonia concentration of 50 µg/L is probably enough to block the free bromine pathways for at least several minutes (Hofmann; 2000). However, it may not be enough to continue to block the pathways for typical ozone contact times of 20 to 30 minutes, depending on the water quality conditions. It may therefore be necessary to add additional ammonia to increase the levels already present. Previous studies have used ammonia doses in the 0.1 to 0.5 mg/L range (Neemann et al. 2004; Buffle et al. 2004).

Ammonia reacts with ozone to block the oxidation of bromide to bromate through a series of complex reactions as shown below (Haag et al. 1984):

$$O_3 + Br^- \rightarrow O_2 + OBr^- \quad (6)$$

$$HOBr \leftrightarrow H^+ + OBr^- \quad (7)$$

$$HOBr + NH_3 \rightarrow H_2O + NH_2Br \text{ (monobromo-amine)} \quad (8)$$

$$3O_3 + NH_2Br \rightarrow 2H^+ + NO_3^- + Br^- + 3O_2 \quad (9)$$

The reaction is negligibly slow at pH values less than about 8, since ozone only reacts with the NH_3 form of ammonia, and not ammonium ion (NH_4^+) (Von Gunten et al, 1994).

The effects of ozone dosage, pH depression and ammonia addition were studied by Ulrich and Von Gunten, 2001. The research showed that for a given Ozone exposure, the OH radical exposure decreases with decreasing pH. Therefore, for pH depression the overall oxidation capacity for a certain ozone exposure decreases, which in turn leads to a smaller bromate formation. Meunier and Von Gunten, 2006, studied the implication of sequential use of ozone and UV for drinking water quality. At low ozone dose of 0.5 mg/L, bromate formation could be kept below 0.4 μg/L. They concluded that the combination of ozone at reduced dosage and UV lamps leads to an improved water quality with regard to MTBE removal and bromate minimization. Diamadopoulos and Tyrovola (2004) suggested that since Ozone decomposes quickly in water, the main variable for efficient disinfection and bromate reduction is the product CT (ozone exposure). The CT value was defined as the product of the time of exposure (minutes) and the residual disinfectant concentration (mg/L) measured at the end of this time (i.e. ozone dose x contact time). They highlighted further that bromate formation increased as the contact time increased under the same ozone dose. Increasing ozone dose while keeping a constant contact time resulted in increasing bromate formation. Manassis and Constantninos (2003) also highlighted the effects of ozone dosage, pH depression and CT in reducing bromate formation in

drinking water. They showed that at an ozone dose of 0.15 mg/L and pH of 7.6, a CT of 10.3 minutes and bromate concentration of 13.5 µg/L were observed, while at pH 7.25, the values of CT and bromate concentration were 12.6 minutes and 9.6 µg/L, respectively. By decreasing the pH further to 6.8, an increased CT value of 15.8 minutes and a reduced bromate concentration of 5.5 µg/L were recorded. Many scientists have also suggested "The chlorine-Ammonia process" as an alternative bromate reduction strategy, where pre-chlorination will be followed by addition of ammonia prior to ozonation. This method has not been fully documented and established in many literatures.

It is however, unfortunate that studies on the treatment of contaminated water using ozone-based AOP technologies in combination with bromate minimization strategies are limited in the literatures. Kruithof et al., (2008); studied the impact of different AOP methods (O_3/UV, O_3/H_2O_2/ and UV/H_2O_2) on Atrazine degradation with emphasis on Bromate formation. Meunier and Von Gunten (2006); studied the implication of sequential use of ozone and UV light for drinking water quality. In the research, they compared the sequential dosage of ozone with UV light for MTBE disinfection while monitoring bromate formation. Manassis and Constantninos (2007); evaluated the combination of UV/H_2O_2 treatment with GAC in MTBE degradation, where they altered the ozone dosage and UV light intensity. The result of the experiment showed no bromate formation.

CHAPTER 3

RESEARCH OBJECTIVES

This study intends to investigate the efficiency of pH suppression and Ammonia addition in controlling bromate formation during the remediation of phenol by ozone-based AOP.

The specific objectives of the work are;

1. To degrade Phenol in water with the most appropriate AOP technique.
2. To assess the extent of Bromate formation under different ozone-based AOP treatment conditions such as UV light intensity, ozone dosage and contact time**.**
3. To study the efficiency of bromate minimization under different levels of pH and Ammonia.
4. To identify the optimum conditions of pH and Ammonia levels to achieve the minimum concentration of bromate in treated water.

CHAPTER 4

RESEARCH METHODOLOGY

All experiments and analysis were conducted at the Centre for Environment and Water (CEW), Research Institute (RI), King Fahd University of Petroleum and Minerals.

4.1 MATERIALS AND METHODS

4.1.1 PHOTOREACTOR

The batch experiments were conducted in the NORMAG® tabular photoreactor with forced liquid circulation as shown in Figure 4.1. The photoreactor consists of a radiation vessel with tempering mantis, cooling tube, immersion tube, Hostaflon® pump circulator, a splash-proof guided counter magnet with flanged driving motor, control unit for driving motor, threaded tube connectors, connecting piece for fumigation frit with spherical ground joint cup and cock, screwed clip, hose connector couplings, clips for spherical ground joint, and thermometer. The photoreactor is mounted on a tripod frame table built up with powder-coated tube connectors. The radiation vessel has a total volume of 400-500 mL. The cooling tube and immersion

tube are made of quartz. In photochemical reaction with UV light, intensive mixing of the reaction solution is particularly important. Transmission of UV light deteriorates with the thickness of the film of solution, so that the substances must be brought into the immediate vicinity of the light source by effective agitation. Therefore, in our setup, the liquid is circulated extremely effectively by the glass pump that is fixed below the reaction vessel.

The reactor has a fully Hostaflon® coated pump rotor. The liquid above the pump is sucked down, thrown outwards by the pump rotor, forced up through the riser pipe and fed back to the reaction chamber through the upper end of the pipe. In addition, the turbulence in the solution created by a magnetic agitating rod is sufficiently intensive. Hence, the UV light is fully utilized due to the thin film of solution and its efficient circulation. The light source most suitable for any specific photochemical reaction depends on the effective spectrum of the substance or system and on the light output.

The UV reactor is equipped with a glass diffuser to purge the ozone in tiny bubbles throughout the contaminated water. The UV reactor is also equipped with an exit connected via a flexible tubing to allow the ozone gas to be vented out. For safety precautions, ozone gas leaving the UV reactor was removed through venting it in an indigo solution. The indigo solution was itself placed inside the fume hood operating under vacuum.

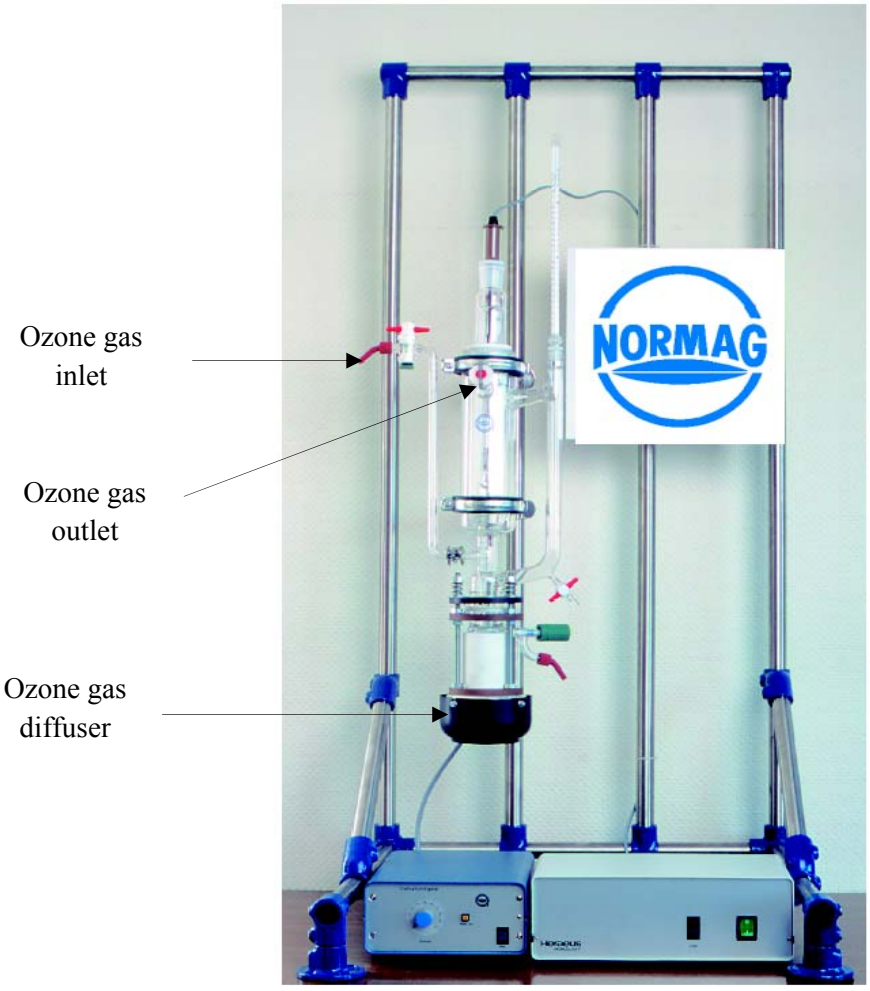

Figure 4.1: NORMAG Photoreactor

4.1.2 UV LAMPS

The Low pressure and medium pressure lamps used in this study (Figure 4.2) were obtained from Heraeus (www.heraeus-noblelight.com). As per the manufacturer, the two lamps operate in the following wavelength range

- Low pressure lamps (LP) emit radiation at a wavelength of 254 nm with intensity of 15 Watts (TNN 15/32, 55 Volts, Cat No. SAA 09370)

- Medium pressure lamps (MP) deliver a broad band spectrum over the complete range of 200 – 300 nm with intensity of 150 Watts (TQ 150, 85 Volts,CatNo.SAA09360).

4.1.3 OZONE GENERATOR

In this study, ozone used in the experimental work was generated using the C-Lasky C-L1010 ozone generator (Figure 4.2) made by Air-Tree Ozone Technology Co. Taiwan. C-Lasky series is designed to provide high efficiency, low energy consumption and stable ozone production. Ozone of C-Lasky series is generated between the surfaces of quartz tubes so that no metallic oxidation contamination can occur. This design does not only improve the efficiency of ozone production but also reduces the maintenance of the ozone generator. This unit has the capability to produce ozone at a rate of 10 g/hr if pure oxygen is used at 6 lit/min and 2 g/hr at 25^{o}C if air is used at 6 lit/min.

Figure 4.2: Lasky C-L1010 ozone generator

4.2 STANDARDS AND REAGENTS

4.2.1 De-ionized Water

De-ionized waters were used throughout the experiment. The water were freshly de-ionized from the Milli-Q Deionizer and stored in clean glass containers.

4.2.2 Phenola

Phenol stock solution was prepared from phenol crystal (99.9% purity), Baker Analyzed. An A.C.S reagent CAS NO: 108-95-2 produced by J.T Baker, U.S.A. 50ppm stock solution was prepared from this 500g crystal and was spiked into the water in the reactor at every batch.

4.2.3 Kalium Bromide (KBr)

Kalium Bromide (KBr) produced by Merck Chemicals (Art. 4907, 500g) was used to prepare the Bromide stock solution of 5mg/L used throughout the study.

4.2.4 Potassium Bromate ($KBrO_3$)

Potassium Bromate ($KBrO_3$ = 167.00) manufactured by BDH chemicals Ltd, Poole, England was used in calibration the IC system for Bromate analysis.

4.2.5 Ammonium Hydroxide

The stock Ammonia solutions spiked into the reactor were prepared from the Ammonium Hydroxide solution, 30% Baker instra-analyzed reagent. CAS No: 1336-21-6. Made in the U.S.A by J.T Baker Chemicals, New Jersey.

4.2.6 Indigo Dye

The Gurr Indigo trisulfonate dye (C.I 73015) used in the quantification and quenching of ozone was manufactured by BDH Chemicals Ltd, England.

4.2.7 Orthophosphoric Acid (H_3PO_4)

Orthophosphoric acid solution (specific gravity 1.75) manufactured by BDH chemicals, England, was used in the determination of ozone in water (indigo method).

4.2.8 Sodium Dihydrogen Phosphate ($NaH_2PO_4.2H_2O$)

Sodium Dihydrogen Phosphate (Mr. 156.01), Fluka AG, Ch-9470, HPLC grade, manufactured by Buchs Ltd was used as part of the recipe in the preparation of buffers for pH's 4, 5, 6 and 7 respectively.

4.2.9 Sodium Sulphite (Na_2SO_3)

50mg/10mL of Sodium Sulphite manufactured by BDH chemicals Ltd was used to quench excess ozone in the treated water before been taken for analysis.

4.2.10 Sodium Hydroxide Pellets

NaOH solution used as part of the recipe for Buffer preparation at all pH levels were prepared from the NaOH pellets (Mr 40.00) manufactured by FLUKA AG, Switzerland.

4.2.11 Sodium hydrocarbonate ($NaHCO_3$)

$NaHCO_3$ (407 K3740323) manufactured by E. Merck Chemicals Ltd was used in preparing the buffered water at pH 9.

4.2.12 Hydrochloric Acid Solution

HCl solution used during the quantification of ozone (indigo method) was prepared from HCl solution (Certified A.C.S plus; A1 44L-212) produced by Fisher Chemicals, NJ, U.S.A.

4.3 ANALYTICAL METHODS

4.3.1 Determination of Ozone in Water

Approximately a dozen analytical methods for determination of aqueous ozone were found in the literature. This study employed the most applauded method which involve the decolorization of indigo trisulfonate at 600nm using the UV/VIS Spectrophotometer (Bader and Hoigne, 1981). This helped in estimating the concentration of ozone that dissolves in water at a specific time. The process involved

preparing a stock solution of aqueous ozone by continuously purging bubbling ozonated oxygen through a gas-washing bottle into distilled water chilled to 2^{o}C. A series of 100mL volumetric flask were filled with 0.5M Phosphate Buffer reagent and 4ml of 1mM Indigo reagent. Ozonated water added to these flasks at Times 0, 5, 10, 20, 30, and 40 minutes and analyzed using the Aquamate UV/VIS Spectrophotometer AQA2000E **(**Figure 4.3).

Figure 4.3: Aquamate UV/VIS Spectrophotometer

4.3.2 Bromate Analysis

In line with the regulations on the allowable limit of bromate in drinking water, a lot of methods have been developed to accurately analyze bromate concentrations in water. Many scientists believe that this limit has been defined primarily on the detection capabilities of existing analytical instrumentations and not on toxicological considerations. This has called for the development of more sensitive alternative

techniques, which have been considered within the past few years. However, accurate measurement of bromate concentrations in water presents difficult problems, the main difficulty being the availability of instrumental methods with a suitable sensitivity. The analytical methods used nowadays have detection limits ranging from 0.1μg/L to 10μg/L. Advanced techniques have been developed to analyze bromate at and below the regulatory limits, with Ion Chromatography (IC), coupled with conductivity detector (IC-CD), post column reaction and Ultraviolet (UV) detection (IC-PCR), or Inductively Coupled Plasma-Mass Spectrometry (IC-ICPMS) in widespread (Ingrand et al., (2000)).

Ray Butler et al., (2005); highlighted different techniques currently available for trace bromate analysis in potable water system, and gave a detailed identification of methodology for routine analysis of bromate in ground and waste water samples. Strategies compared were high performance liquid chromatography (HPLC) with direct UV or PCR/UV detection, IC-PCR, and a simple spectrophotometric technique. The Ion Chromatography with Conductivity Detector (IC-CD) was the most cost-effective solution for simultaneous analysis of bromate and bromide.

In this study, samples collected from the reactor were analyzed by a DIONEX ICS 3000 Ion Chromatography equipped with Conductivity Detector (IC-CD) (Fig. 4.4) 1mL of each sample collected from the reactor was diluted ten times before been analyzed in the IC.

Figure 4.4: The IC System

4.3.3 Phenol Analysis

The concentrations of phenol were determined using the WATERS BINARY HPLC SYSTEM 1525 model equipped with the EMPOWER software, Waters Photodiode Array Detector 2996, and Waters 717-Plus Auto sampler (Fig. 4.5). The system has a reverse phase column of C-18 and an isocratic method with a solvent mixture of methanol-water ratio (40:60) as a mobile phase with the flow rate of 1mL/min. Each vial was filled with 10mL samples and allowed to run for a period of 12minutes.

Figure 4.5: The HPLC System

4.4 EXPERIMENTAL PROCEDURE

The following procedures were followed for the experimental bench scale study:

1. The reactor was charged with approximately 450ml buffered water (depending on the pH), and allowed to warm up to room temperature (20-21^{o} C).

2. The water was spiked with 50ppm phenol and 5ppm bromide stock solutions.

3. Ammonia of known concentrations was added to the reactor prior to ozonation.

4. Ozone was purged from into the reactor for a specific duration equivalent to a known concentration of ozone (Batch Ozonation). Once the required concentration of ozone was reached, the generator was turned off.

5. In the case of continuous ozonation, ozone was continuously purged into the reactor throughout the duration of the experiment at the rate of 1Litre per minute.

6. The UV source was turned on at time T = 0 min.

7. To assess the treatment process, 10ml samples were taken at batches of 0, 0.17, 5, 10, and 20, and 30 minutes respectively. The samples were analyzed for Phenol and bromate concentrations.

4.5 EXPERIMENTAL PLAN

Several experiments were carried out during this period and were mainly focused on investigating the most suitable ozone-based AOP technique for the removal of phenol in water while implementing the bromate minimization techniques using different dosage of ammonia concentrations at different pH levels. The sequence in which all the experiments were conducted is shown in Appendix F. Table 4.1 below show the levels of various parameters used in the experiments:

Table 4.1: Parameters used in the Experiments

AOP Techniques	Bromide (ppm)	Phenol (ppm)	NH_3 (ppm)	UV (Watts)	pH Levels
Batch Ozonation	5	50	0.1	15	4
Continuous Ozonation			0.5	150	5
UV only			1.0		6
tinuous Ozonation/UV			1.5		7
					9

CHAPTER 5

RESULTS AND DISCUSSION

5.1 DEGRADATION OF PHENOL BY OZONE-BASED AOP

5.1.1 DEGRADATION OF PHENOL BY MIXING ONLY

Preliminary experiments otherwise known as Blank runs were conducted at different pH levels (7, 6, 5 and 4) to investigate if there was any removal of Phenol from the water due to processes other than the AOP. Simulated waters were circulated through the UV photoreactor and Phenol was analyzed in the samples after 0, 5.17, 5, 10, 20 and 30 minutes respectively. The results are shown in Figure 5.1. It is clear that no Phenol was removed due to mixing. Moreover, neither Phenol degradation nor bromate formation was detected after mixing the water in the reactor for 30 minutes duration.

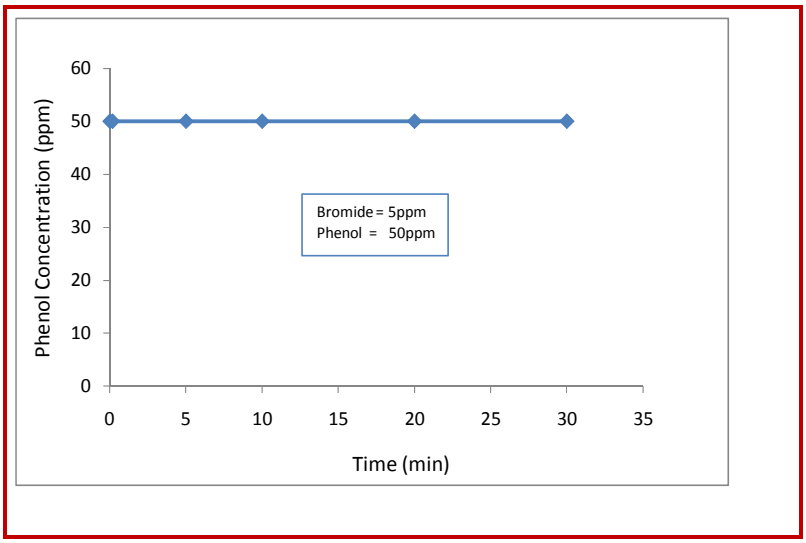

Figure 5.1: Degradation of Phenol from water due to mixing only

5.1.2 DEGRADATION OF PHENOL BY OZONE ONLY

One of the AOP combinations proposed under this study by which phenol will be degraded involved the use of ozone as the only oxidising agent. Ozone combined with hydrogen peroxide or UV light will generate the hydroxyl radicals that have the capability to degrade organic contaminants such as MTBE (Tawabini et al., 2007 and 2008). In the meantime, ozone by itself is known to be a strong oxidant and has been shown to have the ability to degrade Phenol alone (Kadir et al., 2008). To investigate this assumption, numerous experiments were conducted using ozone only at different pH levels and different ozonation methods i.e. batch ozonation (10ppm ozone) and continuous ozonation.

5.1.2.1 Degradation of Phenol by Batch Ozonation Only

Four hundred and fifty (450) mL buffered water of different of pH levels were purged with ozone gas for 20 minutes, which was found to be the time needed to generate 10 ppm ozone (indigo method). The ozone generator was turned off after the 10 ppm required concentration was attained, and the water was immediately spiked with 5 ppm Bromide and 50 ppm Phenol stock solutions. Samples collected were analyzed for phenol concentrations. The results are plotted in Figure 5.2

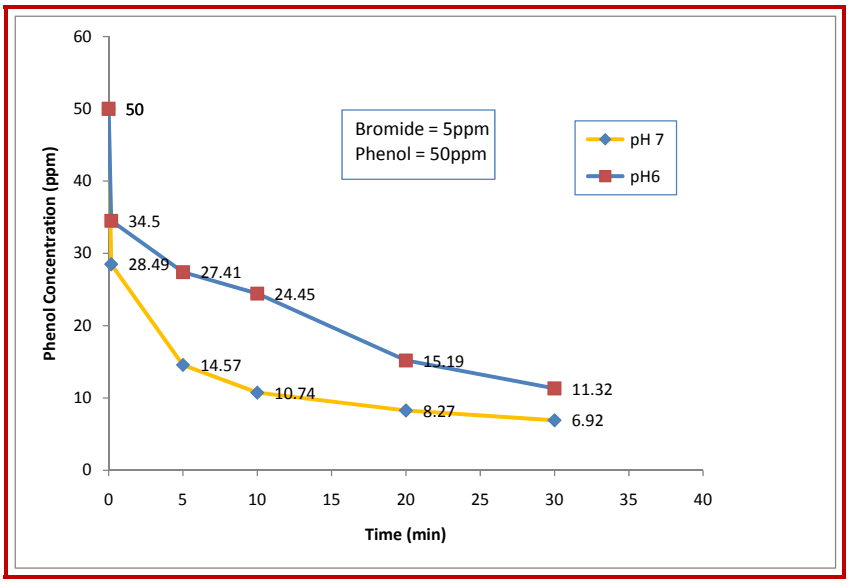

Figure 5.2: Degradation of Phenol by Batch Ozonation Only (10ppm).

Figure 5.2 show that 10 ppm of ozone, when used alone could not completely degrade phenol in water. These results also show that the degradation of phenol using batch ozonation is pH dependent. Phenol degraded from 50 ppm to 6.92 ppm at pH 7 and to 11.32 ppm at pH 6 after 30 minutes. This is equivalent to 86.8% and 77.4% removal

of phenol by batch ozonation (10 ppm ozone) at these two pH levels. This incomplete degradation could be due to the consumption of the 10 ppm ozone by the bromide ions, hence there was no more ozone to continue the degradation of phenol after the 30 minutes period.

5.1.2.2 Phenol Degradation by Continuous Ozonation Only

Following the results obtained from the batch (10 ppm) ozonation, it became imperative to investigate the efficiency of continuous ozonation method, which involves a continuous and steady purging of ozone into the reactor throughout the duration of the experiment. This has been proved to be more effective in the literature (Wu et al., 2000; Kadir et al., 2007). To achieve this, the reactor was continuously ozonated at the rate of one liter per minute (1 L/m) for a period of 30 mins. Samples were collected at specific intervals and analyzed for phenol concentrations. Figure 5.3 show the result of the experiments.

Unlike the batch ozonation (10 ppm Ozone), continuous ozonation at the rate of one litre per minute completely degraded phenol from 50 ppm to 0 ppm (100% removal) in less than 5 minutes at all pH levels (6 and 7). These results show that continuous ozonation is not only effective in degrading phenol completely but it does so within a very short period of time (less than 5 minutes) irrespective of the pH of the water.

Figure 5.4 shows the comparison between these two ozonation methods with regards to phenol removal.

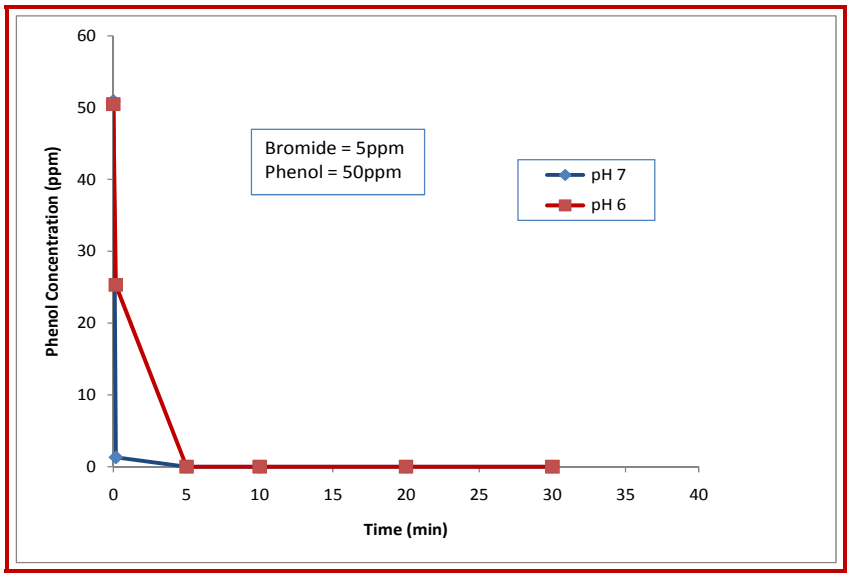

Figure 5.3: Degradation of Phenol by Continuous Ozonation Only

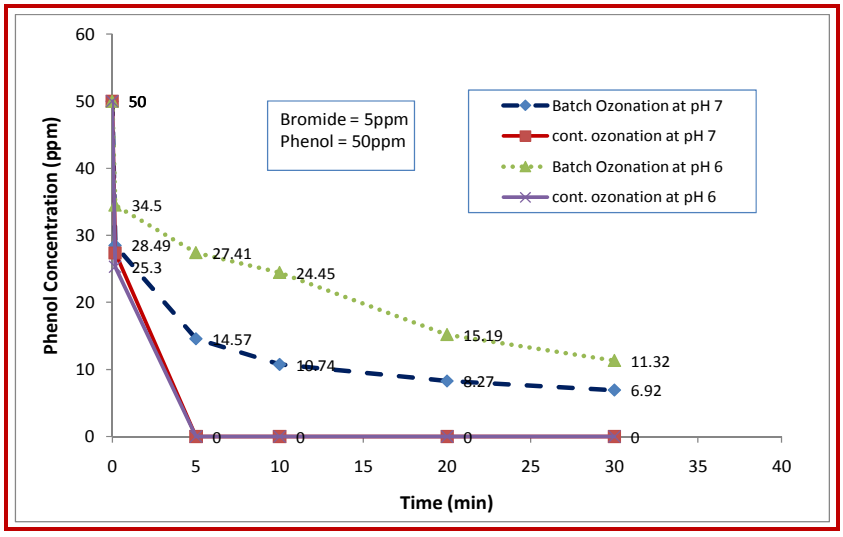

Figure 5.4: Degradation of Phenol by Batch and Continuous Ozonation methods

5.1.2.3 Degradation of Phenol by Continuous ozonation at different pH Levels

To verify the result that showed that continuous ozonation at 1 litre per minute is not pH-dependent, the study investigated the degradation of Phenol at different pH levels (4, 5, 6 and 7). The results obtanied are plotted in Figure 5.5.

The results illustrated in Figure 5.5 indicate that continuous ozonation is capable of removing phenol from water regardless of the pH in less than 5 minutes.

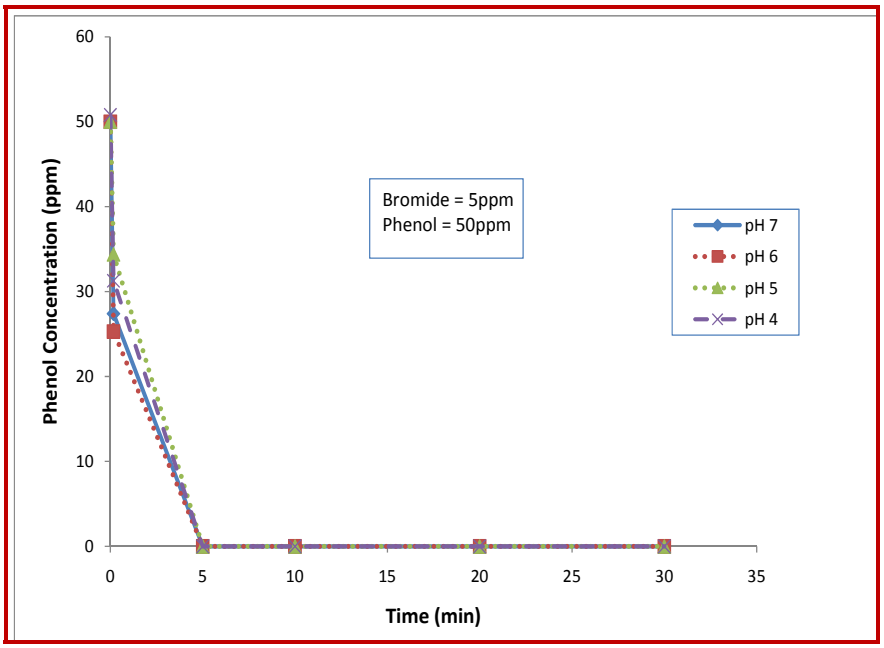

Figure 5.5: Effects of Continuous ozonation on Phenol degradation at different pH

5.1.2.4 Effects of Continuous Ozonation on Bromate Formation

Having shown that continuos ozonation at the rate of 1 litre per minute is more effcective in the removal of phenol compared to batch ozonation (10 ppm), a series of expriments were conducted to investigate the level of bromate formation using the continuous ozonation method. The experiments were conducted by continuously purging ozone for a duration of 30 minutes into the reactor that was initially spiked with 50 ppm phenol and 5 ppm bromide concentrations. Samples were collected at regular intervals, the residual ozone in the samples were quenched with sodium sulfite and the bromate concentrations in the water were analyzed with the IC.

The results of the experiments show that bromate formation reduces with decreased ozonation. Figure 5.6 show the details of the results obtanied. These results correspond with the findings available in the literature (Von Gunten et al., 2001; Von Gunten and Meunier., 2006; Diamadopoulos and Tryovola., 2004). Westeroff et al, 1998; described this phenomenon by explaining how increased pH level causes rapid decomposition of ozone which will automatically result in more $OH^{\bullet}$ radical generation, and thus increased bromate formation. pH is related to $OH^{\bullet}$, which can be shown in the indirect bromate formation mechanism (Section 2.3).

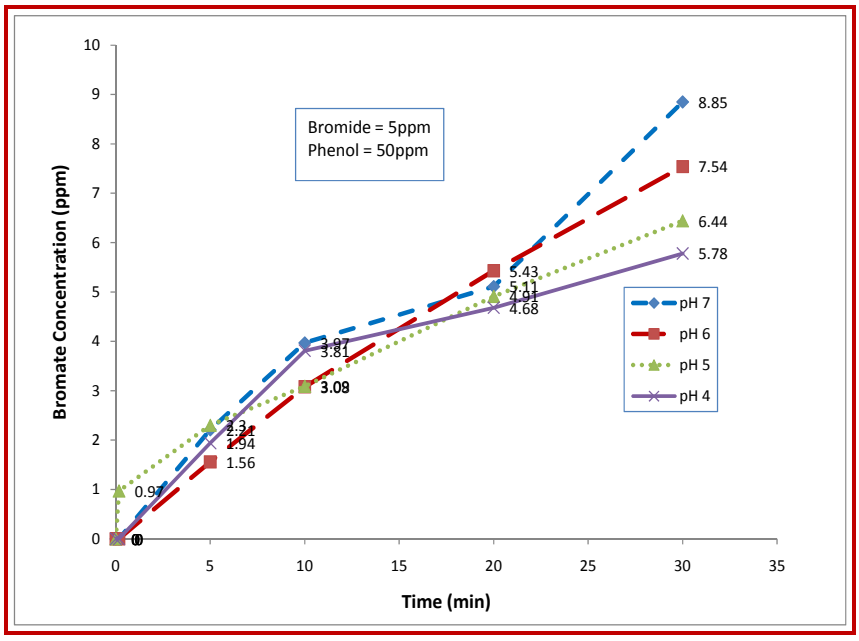

Figure 5.6: Effects of Continuous Ozonation (1 liter per min.) on Bromate Formation at different pH levels

5.1.3 DEGRADATION OF PHENOL BY UV ONLY

Many of the organic compounds that absorb UV light are expected to degrade to a certain extent depending on many factors such as molecular structure of the compound, light wavelength and intensity, duration of exposure, absorption of the compound…etc. The characterization of the two UV lamps used showed that the LP lamp produces spectrum mainly at 254 nm and it can be described practically as monochromatic since the other lines in the UV and visible regions radiate very faintly in comparison to the 254 nm line (Tawabini et al., 2008). The MP lamp emits light

with intensity of 150 Watts with its characteristics mercury line system extending from the short-wave UV range of about 240 nm well into the visible region. Within this range, there are several intense and a number of weaker lines. In fact, it was shown that MP lamp of the photo-reactor (150 Watts) gives much weaker intensity at the wavelength 254 nm, but it has significant UV peaks at higher wavelengths including 365 nm (Tawabini et al., 2008). It also emits very strong peaks within the visible-region. It was therefore highly expected that such lamp would not produce good amount of hydroxyl radicals and may play other uncontrolled roles within the photochemical oxidation process.

Thus, it was necessary at this stage to explore the extent of degradation of Phenol after being exposed to these UV light sources. In two experiments, simulated water samples were exposed to two different UV light sources only, namely: 15 Watts low pressure (LP) and 150 Watts medium pressure (MP) sources. Samples taken were analyzed for phenol and bromate concentrations respectively. Results of the analysis are shown in Figures 5.7, 5.8 and 5.9 respectively. These figures show that partial degradation of Phenol occurred as a result of exposure to UV light sources only. This indicates that Phenol could be partially but not completely degraded by UV photolysis. However, higher degradation of Phenol was observed when exposed to the MP rather than the LP. Approximately, after 30 minutes of exposure, 18% of Phenol was removed when exposed to the LP 15 Watts UV source compared to more than the 50% removed when exposed to the MP 150 Watts UV source i.e. Phenol

degraded from 50 ppm to 40.95 ppm with LP 15Watts Lamp and to 22.92 ppm with the MP 150 Watts Lamp.

Figure 5.9 shows the combined effects of the two lamps on Phenol degradation and in both cases, there was no bromate formation. These results confirm that Irradiation with UV lights does not contribute to bromate formation. UV is in fact, used for bromate control (Beckles et al.; 2006). The three figures (5.7, 5.8 and 5.9) also show a higher photolysis and thus higher degradation rate of phenol in the case of 150 Watts MP Lamp. The heat emitted from the UV lamps was controlled by the jacket of water passing through a water bath. The temperature only varied between 21°C to 23°C throughout the 30 minutes run. Thus, it is less likely that Phenol was removed more in the case of MP due to higher temperature but more due to effects of photolysis.

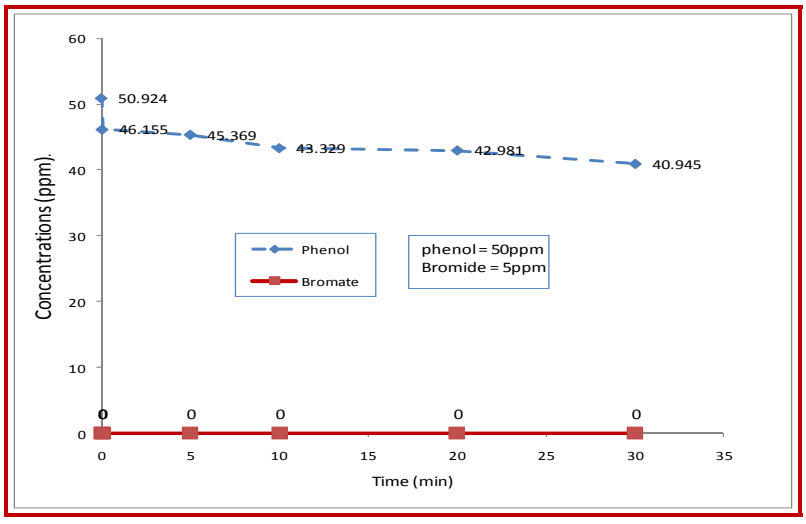

Figure 5.7: Effects of 15 Watts LP on Phenol Degradation and Bromate Formation

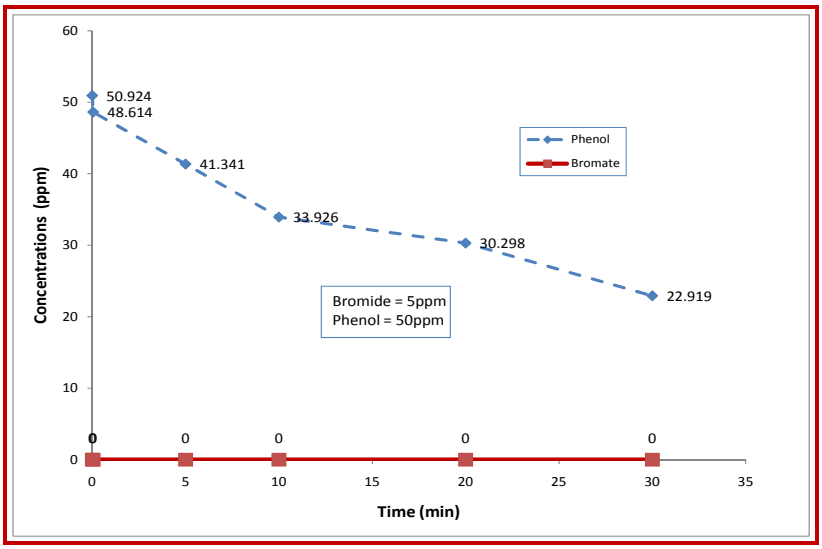

Figure 5.8: Effects of 150W MP on Phenol Degradation and Bromate Formation

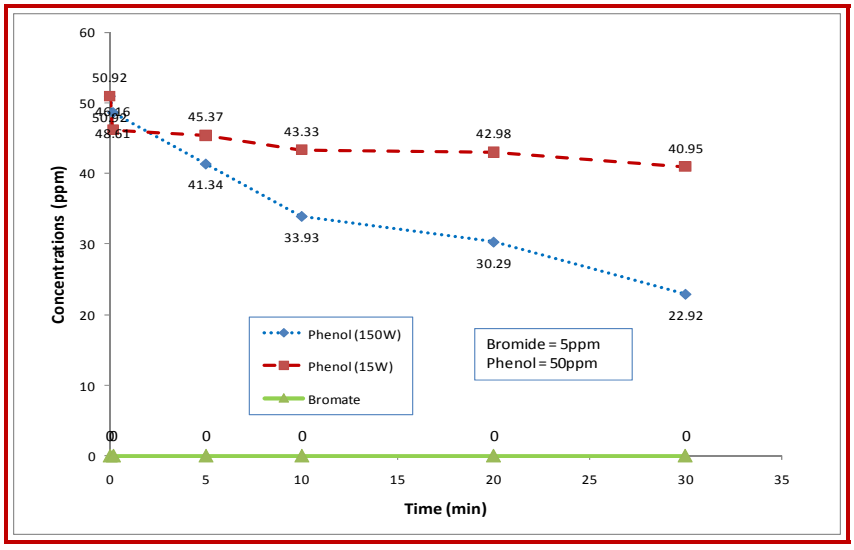

Figure 5.9: Effects of 15 Watts and 150 Watts UV on Phenol Degradation and Bromate Formation

5.1.4 DEGRADATION OF PHENOL BY UV/OZONE PROCESS

After several runs made with ozone only and the problem encountered with regards to incomplete degradation of Phenol with the Batch (10 ppm) Ozonation, the research work was focused on the AOP process that depends on the combined effects of UV and ozone to produce the hydroxyl radicals needed to degrade the contaminant (Phenol). The aim of trying out different Ozone-based AOP method was to find the most appropriate, most practicable and the least expensive method of removing Phenol in water. In this part of the bench-scale study, several treatment runs with the 15 Watts UV LP and 150 Watts MP sources were combined with the continuous ozonation at the rate of one liter per minute, which was earlier shown to be more result-oriented than the batch ozonation (10 ppm ozone).

5.1.4.1 Degradation of Phenol by LP 15 W UV/Ozone

Bench-scale experimental runs were conducted at different pH levels where the LP 15 Watts UV source was used to irradiate the simulated water in the reactor while continuously purging ozone at the rate of 1 liter per minute. It was observed that phenol completely degraded from 50 ppm to 0 ppm within 5 minutes at all pH levels as shown in Figures 5.8 and 5.9 when continuous ozonation only was used. This is in contrary to the result obtained when 15Watts LP lamp was used alone, where phenol was only able to degrade to 40.95 ppm after 30 minutes. This implies that the 15 Watts LP Lamp is not sufficient at completely removing phenol in water. The complete removal of phenol in less than 5 minutes with 15 Watts UV/Continuous

ozonation was the same with the scenario observed when Continuous ozonation was used alone. This shows that the complete removal of phenol with the 15 W UV/Continuous ozonation was as a result of the oxidation from the continuously purged ozone. The continuous ozonation must have complemented the effects of the 15 Watts LP UV lamp which previous experiment showed to be ineffective in removing Phenol individually (UV only). Figures 5.10 and 5.11 give a graphical illustration of the effects of this experiment on Phenol removal and bromate formation.

Figure 5.11 shows the level of bromate formation with 15W UV/Ozone, which is almost the same level of bromate formed when continuous ozonation was used alone. This indicates that bromate formation through ozonation dominates the pathway by Ozone/UV. In fact, UV should even lower the rate of bromate formation.

5.1.4.2 Degradation of Phenol by MP 150W UV/Ozone

The selection of the type and intensity of the UV source to produce the needed hydroxyl radical is of prime importance in the AOP process. After investigating the effects of 15 Watts UV/Ozone, it was decided to study the efficiency of the 150 Watts/Ozone on the removal of Phenol and compare the results with those obtained using the LP 15 Watts UV/Ozone method discussed in the previous section.

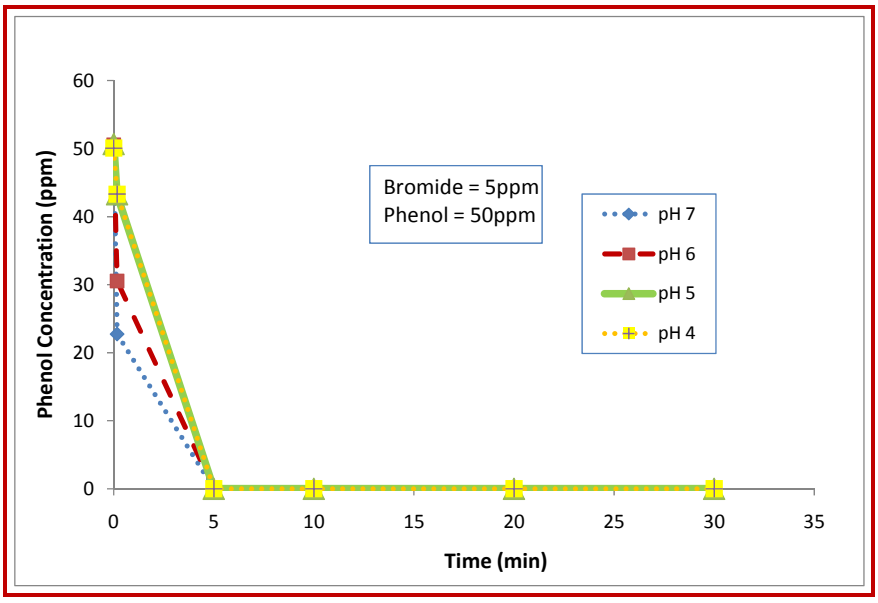

Figure 5.10: Effects of 15 Watts UV/Ozone on Phenol Degradation at different pH levels

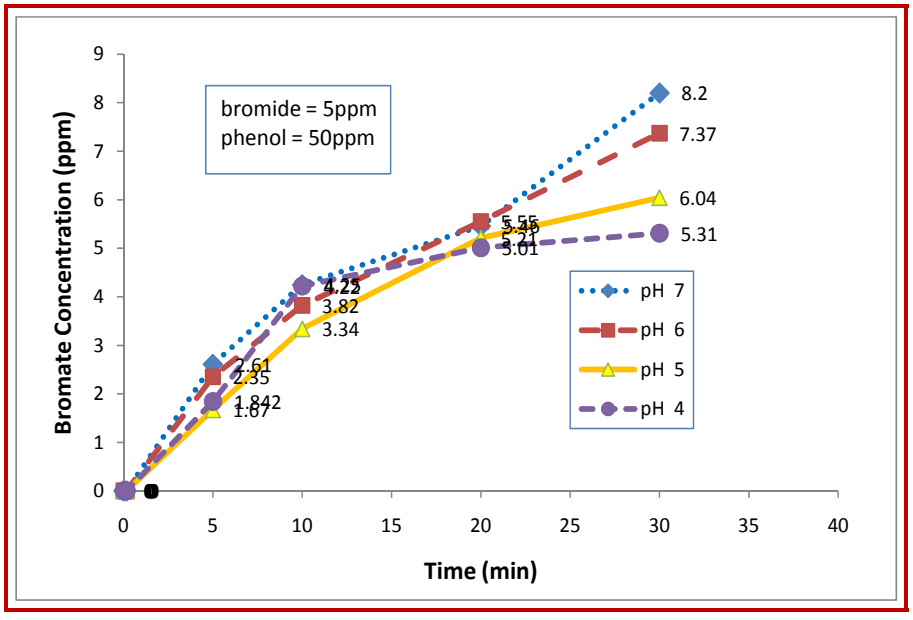

Figure 5.11: Effects of 15 Watts UV/Ozone on Bromate Formation

A number of experiments were conducted to explore the suitability of the MP UV lamp in combination with continuous purging of ozone at different pH levels. Figures 5.12 and 5.13 reveal the effects of MP 150 Watts UV and continuous ozonation (1 liter per minute) on phenol degradation and bromate formation. Similar to the case of 15 Watts UV/Ozone, there was complete degradation of phenol within 5 minutes at all the pH levels. While MP 150 Watts alone was only able to degrade phenol to 22 ppm after a period of 30 minutes (Fig. 5.8), phenol was completely degraded when MP 150W lamp was combined with continuous ozonation.

It is obvious that the complete removal was due to the efficiency of the continuous ozonation method which has proved to be effective in totally removing phenol within 5 minutes (Fig. 5.5) when used alone.

Interm of Bromate Formation, Figure 5.13 shows the level of bromate formed at all the pH levels, which is almost the same concentrations of bromate formed when continuous ozonation was used alone (Fig. 5.6).

Figure 5.14 is gives a comprehensive summary of all the AOP techniques with regards to phenol degradation and bromate formation at pH 6.

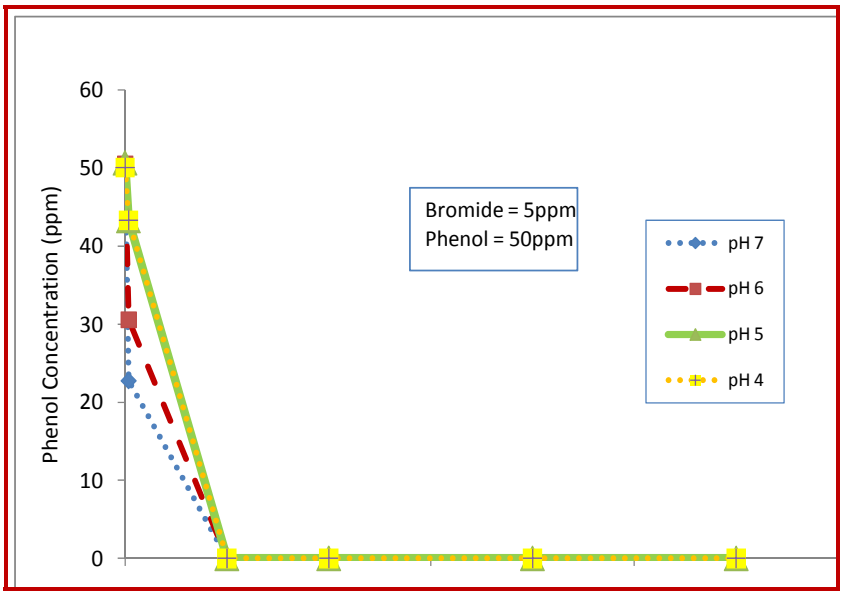

Figure 5.12: Effects of 150 Watts UV/Ozone on Phenol Degradation

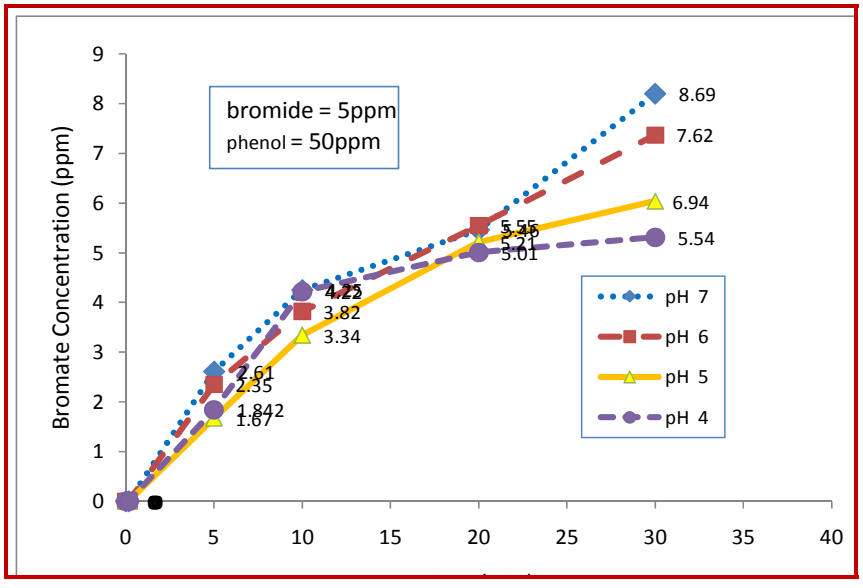

Figure 5.13: Effects of 150 Watts UV/Ozone on Bromate Formation

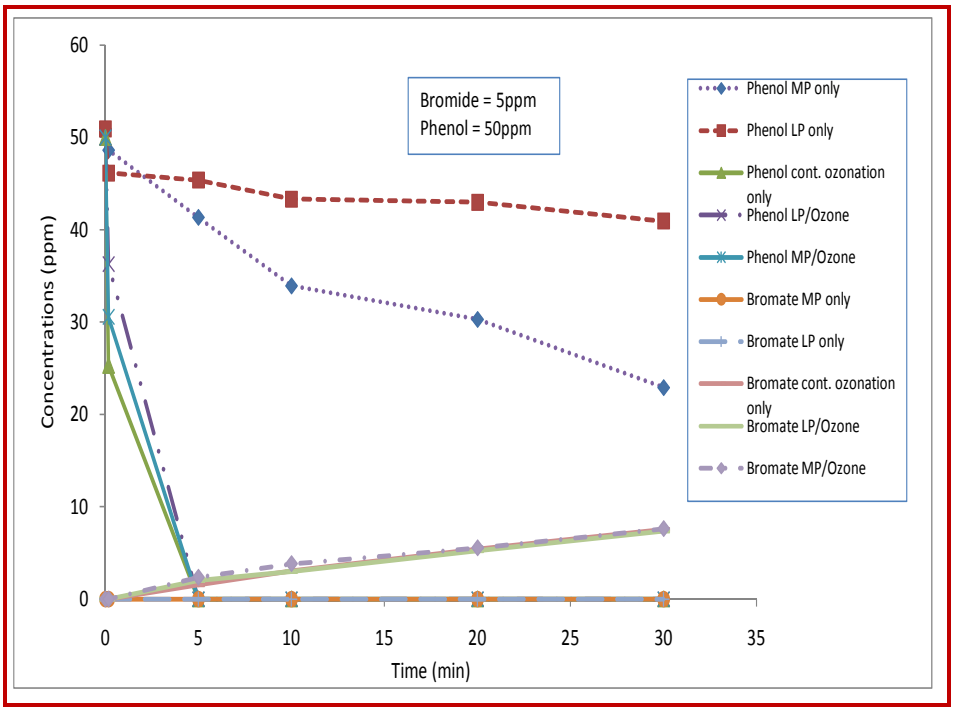

Figure 5.14: Phenol Degradation and Bromate Formation with all AOP techniques at pH 6

5.1.5 REMOVAL OF PHENOL BY STRIPPING EFFECTS

Having compared the efficiency of different Ozone-based AOP techniques in degrading phenol in water, it became necessary to conduct an experiment to assess the removal of phenol due to stripping effects. This is to be sure whether the degradation was due to the ozonation or any other factor, most importantly, the stripping effects.

An experiment was conducted by which an inert gas (N_2) was purged into the photoreactor containing phenol-contaminated water (50 ppm phenol) at the same flow

rate used with the continuous ozonation experiments (one liter per minute). This experiment is particularly important when ozonation step is needed for the removal of organic compounds in water as part of the AOP process. Samples were collected at 0, 0.17, 5, 10, 20, and 30 minutes and analyzed for Phenol Concentrations.

The results are plotted in figure 5.15 which shows clearly how Phenol concentration decreased from 5 0ppm to 46.03 ppm after 30minutes. This is equivalent to 8% removal after 30 minutes. Only 5% removal (47.5 ppm) of phenol was observed in the first 5minutes; the time needed to completely degrade Phenol when Continuous ozonation only and/or in combination with the UV lamps were used. This insignificant reduction in the concentration of phenol by stripping shows that the degradations observed with Ozone only and Ozone/UV were as a result of ozonation effects and not stripping or volatilization. Also, the degradation by-products observed during the removal of phenol by Ozone only, and ozone/UV were not detected with the stripping experiment. This confirmed that phenol did not degrade when purged with the inert gas (Nitrogen).

In Summary, all results indicate that purging ozone (O_3) continuously into the reactor at the rate of one liter per minute will lead to complete degradation of phenol within 5minutes irrespective of the pH of the water. Dosing the water with 10 ppm ozone (batch ozonation), prior to spiking with phenol and bromide solutions was not only found to be ineffective in degrading phenol, but not practicable and pH dependent

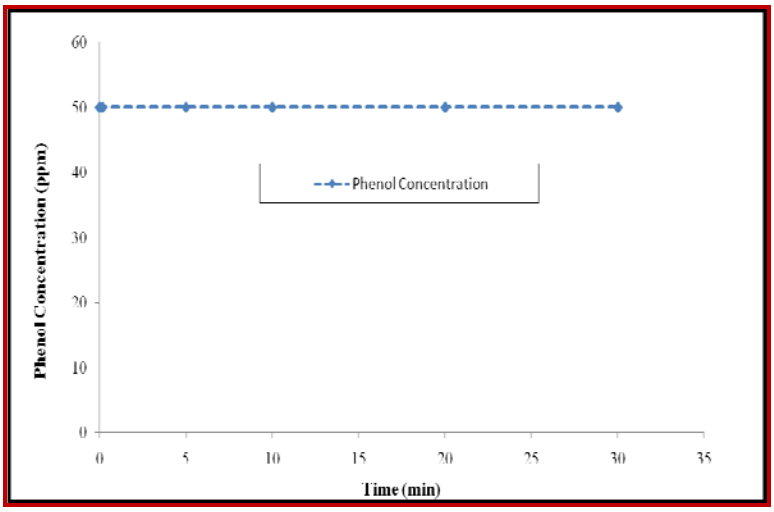

Figure 5.15: Removal of 50ppm Phenol by Stripping Effects.

The two UV lights (15 W and 150 W), although did not contribute to bromate formation, they did not show any appreciable efficiency towards the degradation of phenol when used alone. The focus was then directed towards optimizing the UV/Ozone processes. The results showed that UV/Ozone will degrade phenol within the same time (5 minutes) at which Ozone only (continuous ozonation) will also remove the contaminant in the water.

Also, the use of UV/Ozone will be more much expensive compared to the cost of implementing the continuous ozonation only. The results obtained in this part of the bench scale study were very important to explore the roles of each of the AOP parameters on the treatment effects.

The reactions of phenol with ozone lead to the formation of some by-products. These by-products were the same as those highlighted by Kadir et al., 1998. Appendix E

gives a chromatographic view of phenol and the associated by-products of its degradation. The by-products were:

1. Catechol (C).
2. Hydroquinone (HQ).
3. Para-benzoquinone (PBQ).
4. Ortho-benzoquinone (OBQ).

Based on the aforementioned findings, subsequent experiments geared towards reducing bromate formation by adding Ammonia into the water were conducted with Continuous Ozonation which previous experiments have shown to be the fastest, the more effective and the least expensive Ozone-based AOP technique in degrading phenol.

5.2 BROMATE CONTROL METHODS

All experiments conducted so far have been focused on elucidating the appropriate Ozone-based AOP method for the remediation of phenol in water. The research at this juncture is now directed at finding the optimum bromate minimization strategy to control bromate formation during the degradation of phenol. As shown in the surveyed literatures, addition of Ammonia to an ozonated water containing bromide could minimize/prevent bromate formation. pH suppression was also shown in many publications to be another effective strategy when combined with Ammonia addition,

to inhibit the oxidation of bromide to bromate in a water treated by ozone-based AOP.

This study decided to investigate these assertions by conducting several AOP experiments in which different Ammonia concentrations were added into the reactor containing buffered water at different pH levels.

5.2.1 Effects of pH Adjustment on Bromate Minimization

The study began by studying the effects of pH adjustment on the minimization of bromate formation from the bromide ions. Several experiments were conducted at different pH levels by continuously purging ozone to the phenol and bromide simulated waters at the rate of one liter per minute in the photoreactor. The experiments commenced with a high a pH level (pH 7) and subsequent experiments were conducted by adjusting the pH from 7 to 4 respectively. In all of these experiments, the extent of bromate formation and minimization were adequately noted. Figure 5.16 shows the results obtained.

From the plot, it can be seen that the concentrations of bromate reduced with decreased pH. A transition from pH 7 to pH 6 led to a 15% reduction in bromate formation. Further suppression to pH 5 led to a 27% reduction in the concentration of bromate. At pH 4, the concentration of bromate formed during the ozonation of bromide containing water had significantly reduced to 5.78 ppm, which is equivalent to 35% reduction in bromate formation.

Although 5.78 ppm of bromate is far beyond the allowable bromate concentration in drinking water (10 ppb), the results of these experiments have shown that adjusting the pH can significantly reduce the concentrations of bromate ions that will be formed.

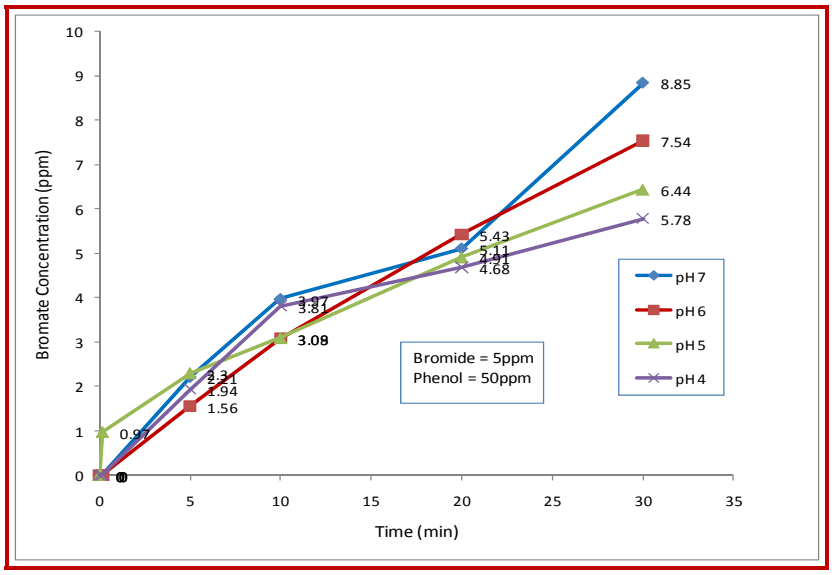

Figure 5.16: Effects of pH Adjustment on Bromate Minimization

This is in conformity with what is documented in the literature, where it has been previously shown that suppressing the pH can significantly reduce the amount of bromate formed. Many reasons have been highlighted for this phenomenon. Von Gunten et al., (1992), explained that the reaction pathways involving O_3/BrO_3^- is higher than that of O_3/HOBr. Thus, bromate formation under basic conditions will be higher than expected in acidic medium. At high pH level, there is more rapid decomposition of ozone, resulting in more OH radical generation, and thus increased bromate formation (Yates and Stensrom, 1993; Westerhoff et al., 1998).

5.2.2 Bromate Control by Ammonia Addition

In this section, the research was focused on the effects of different ammonia concentrations on the minimization of bromate formation. This was conducted using Ammonia concentrations of 0.1, 0.5, 1.0 and 1.5 ppm respectively at different pH levels. The aim was to identify the optimum ammonia concentration and pH level needed to inhibit bromate formation during the implementation of ozone-based AOP in the remediation of contaminated waters.

5.2.3 Effects of 0.1ppm Ammonia on Bromate Minimization

The most widely reccomended ammonia concentration in the limited publications available on the control bromate formation during AOP treatment of contaminated water is 0.1 ppm (Hoffman et al, 200; Von Gunten et al, 2004; Beckles et al, 2006). Hulsey et al., (2003), in their patented publication stated categorically that an ammonia dosage of 0.1 ppm should normally be sufficient to meet the bromate formation goal of less than 5 pp b in water. Based on these facts, this study decided to investigate the impact of this ammonia dosage on Saudi Arabian water which has been found to contain 5 ppm bromide (Tawabini et al, 2007). The results of the experiments are plotted in Figure 5.17.

Due to the high bromide content of Saudi Arabian gorundwater (5 ppm), which is considerably high compared to the bromide level at which bromate formation was controlled with 0.1 ppm Ammonia in the publications surveyed, an Ammonia dosage of 0.1 ppm was found to be ineffective in preventing bromate formation. Although, the amount of bromate formed with this ammonia dosage was lower than that formed when when ammonia was not added to the treated water at all.

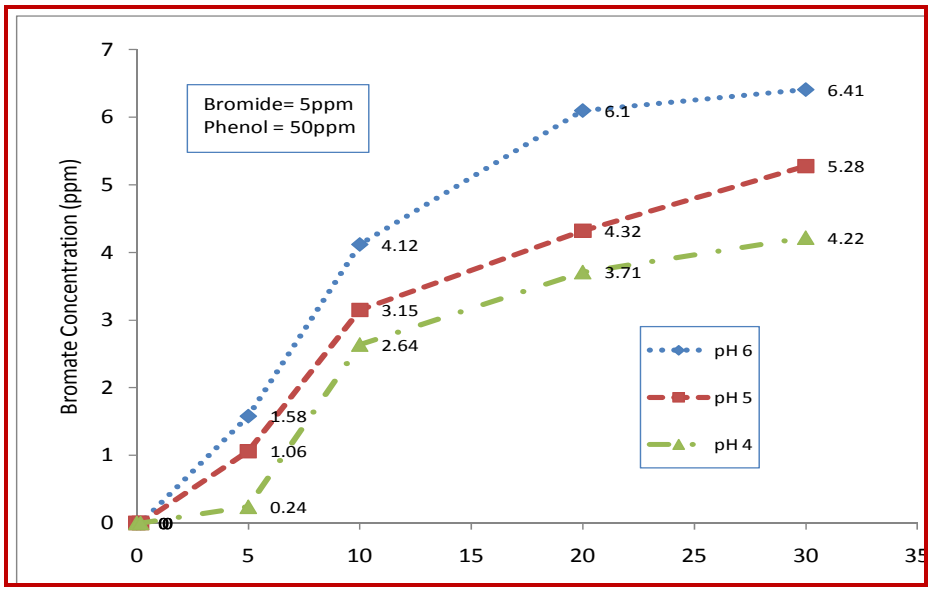

Figure 5.17: Effects of 0.1ppm Ammonia on Bromate Minimization

5.2.4 Effects of 0.5ppm Ammonia on Bromate Minimization

The results obtained from the addition of 0.1 ppm Ammonia which is the most widely reccomended ammonia concentration for bormate control, revealed the ineffciency of lower ammonia dosage in preventing bromate formation. The study proceeded to verify the efficency of 0.5 ppm Ammonia, which is considerably a higher dosage compared to 0.1 ppm. According to Hulsey et al., (2003), a maximum dosage of 0.5 ppm should completely inihibit bromate formation in water.

The results of the experiments are shown in Figure 5.18. It was noticed that addtion of 0.5 ppm ammonia could only minimize bromate formation but not prevent it.

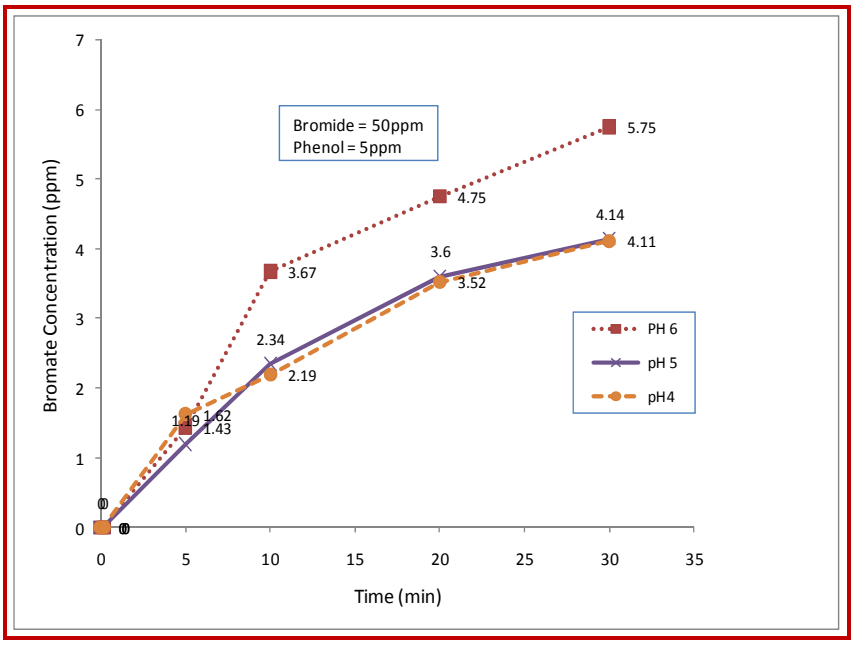

Figure 5.18: Effects of 0.5ppm Ammonia on Bromate Minimization

It was noticed that addtion of 0.5 ppm ammonia could only minimize bromate formation but not prevent it. At pH6 for instance, 5.75 ppm of bromate was detected after 30 minutes, while 6.41 ppm was recorded at the same pH after 30minutes when 0.1 ppm Ammonia was added. This is an equivalent of 10% reduction in bromate formation due to the increment in the ammonia concentration. About 22% reduction in bromate formation occurred at pH5 when the concentration of ammonia added was increased to 0.5 ppm from 0.1 ppm. These results shows that, a futher increase in the ammonia dosage would result in significant reduction in bromate formation. With regards to Phenol, there was complete degradation of Phenol after 5 minutes into the experiment at all the pH levels.

5.2.5 Effects of 1.0ppm Ammonia on Bromate Minimization

The outcome of the experiments conducted with 0.1 ppm and 0.5 ppm necessitated the need to go for a higher ammonia level. In the previous sections, addition of 0.5 ppm ammonia gave significant though unsatisfactory reduction in the amount of bromate formed. This gave an inkling that going for a higher ammonia level would give a more satisfactory result.

At this juncture, the study utilized an ammonia dosage of 0.5 ppm at different pH levels to investigate its efficiency in minimizing bromate formation. The results obtained are plotted in Figure 5.19 where 1.0 ppm ammonia proved to be more efficient in minimizing bromate formation than the previously used 0.5 ppm and 0.1 ppm ammonia respectively. At pH6, 1.0 ppm Ammonia was able to reduce bromate formation from 5.75 ppm to 4.90 ppm after 30 minutes. This is about 15% reduction. A similar trend was observed at pH5 and pH4 respectively, where 1.0ppm ammonia reduced bromate formation by 39% and 62% after 30minutes. Although, the concentrations to which bromate ion formation was reduced are significant, yet they are still above the allowable bromate concentration in drinking water (10 ppb).

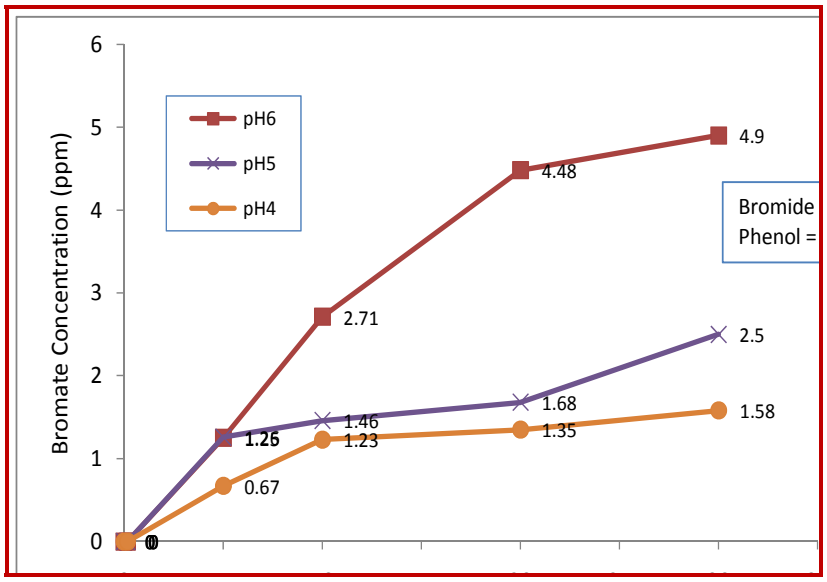

Figure 5.19: Effects of 1.0ppm Ammonia on Bromate Minimization.

5.2.6 Effects of 1.5 ppm Ammonia on Bromate Minimization

Following previous results which showed that increasing ammonia dosage lead to reduced bromate formation; it became imperative to further investigate the effects of a higher ammonia level on minimizing bromate to the allowable standard, which is the objective of this research. An ammonia dosage of 1.5 ppm was investigated at pH6, pH5 and pH4 respectively, where it gave a 100% (0 ppm bromate) reduction in bromate formation, i.e. no bromate was detected at all.

These results prompted this study to go to pH 7, which is a higher pH level which previous experiments showed to favor higher bromate formation. The results of all the experiments are plotted in Figure 5.20. From the plot, it will be observed that with the exception of pH 7, there was no bromate formation at other pH levels. This

indicates that an addition of 1.5 ppm of Ammonia to ozonated water is capable of preventing bromate formation at pH levels below the ambient pH (pH 7).

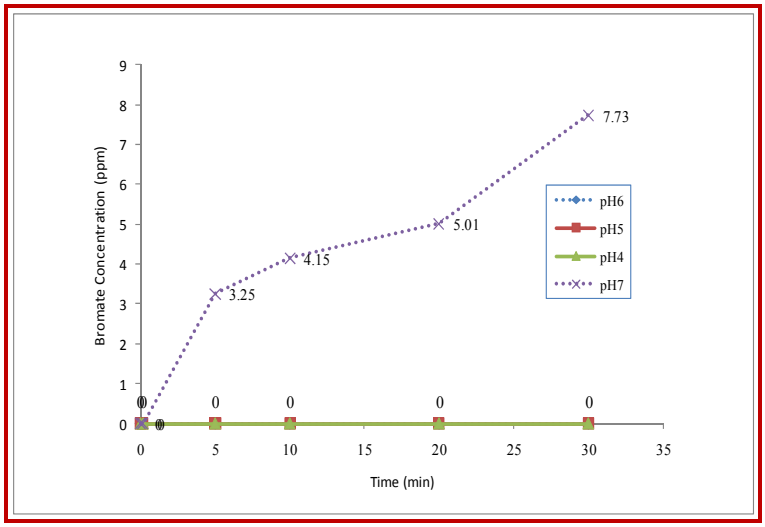

Figure 5.20: Effects of 1.5ppm Ammonia on Bromate Minimization

5.3 OPTIMIZATION OF BROMATE CONTROL

All experiments conducted in the previous section basically reflects the efficiency of ammonia addition at minimizing and/or inhibiting bromate formation at different pH levels. The following plots give a clearer picture of what actually transpired at indivdual pH levels with addition of different ammonia concentrations. This is to ensure a proper assessment of efficiency of different ammonia concentrations at each pH level with regards to bromate formation.

Experiments conducted without controlling bromate formation (ozonation only) at this pH 4 produced 5.78 ppm of bromate ions after 30 minutes, i.e. without adding ammonia. With an addition of 0.1 ppm ammonia, bromate formation dropped to 4.22 ppm after 30 minutes. This is about 27% reduction in bromate formation. A more higher 0.5 ppm concentration of ammonia gave 29% reduction in bromate formation whie 1.0 ppm ammonia minimized the oxidation of bromide to bromate by 73%. There was no detection of bromate ions with an ammonia dosage of 1.5 ppm (100% reduction), while other lower ammonia concentrations produced bromate. Figure 5.21 summarizes the efficiency of different ammonia concentrations in minimizing bromate formation at pH 4.

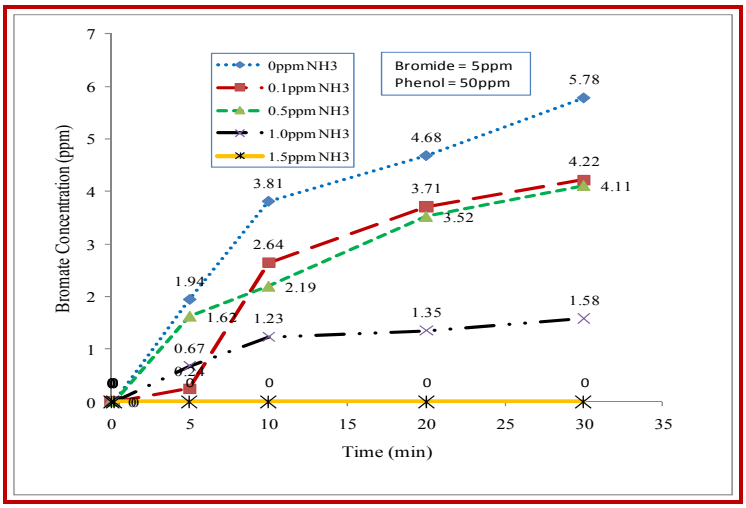

Figure 5.21: Effects of Ammonia on Bromate Minimization at pH4

At pH 5, There was no bromate formation with 1.5 ppm Ammonia, while 2.5 ppm, 4.14 ppm and 5.28 ppm of bromate concentrations were detected after 30 minutes

with 1.0 ppm, 0.5 ppm and 0.1 ppm Ammonia addtion respectively. Figure 5.22 shows the varriations in bromate formation at this pH as ammonia level increased. Only an addition of 1.5 ppm Ammonia inhibited the formation of bromate completely (100% bromate minimization), while other ammonia dosage were only able to reduce bromate but could not prevent its formation. An addition of 1.0 ppm of Ammonia reduced bromate formation by 61%, while 0.5 ppm and 0.1 ppm reduced bromate by 35.7% and 18.1% respectively. This shows that the efficency of ammonia in reducing the formation of bromate increases with increased level of ammonia. The results of this experiment was previously shown in Figure 5.20 (Effects of 1.5 ppm ammonia on bromate minimization).

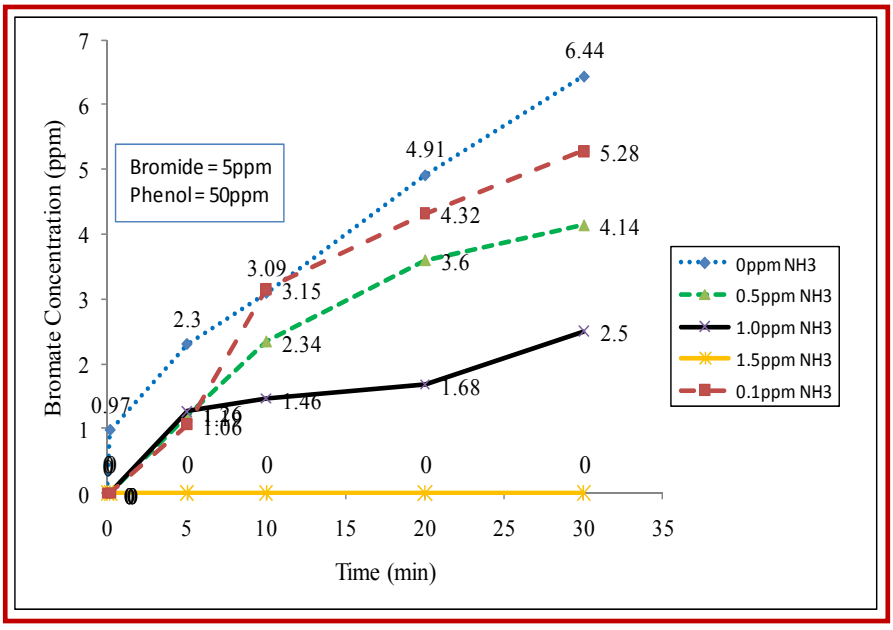

Figure 5.22: Effects of Ammonia on Bromate Minimization at pH5

The results followed a similar trend at pH 6 where 1.5 ppm Ammonia completely prevented the formation of bromate while other lower ammonia levels could only minimize it below the baseline (Figure 5.23)

At pH 7, addition of 1.5 ppm ammonia that had proved to be effective in completely controlling bromate formation at lower pH levels was not sufficient to inhibit the oxidation of bromate from bromide ions. There was only about 13% reduction in bromate formation compared to the baseline level (No Ammonia addition). Figure 5.24 provides an explanation to the effects of Ammonia addition in minimizing bromate formation at pH 7.

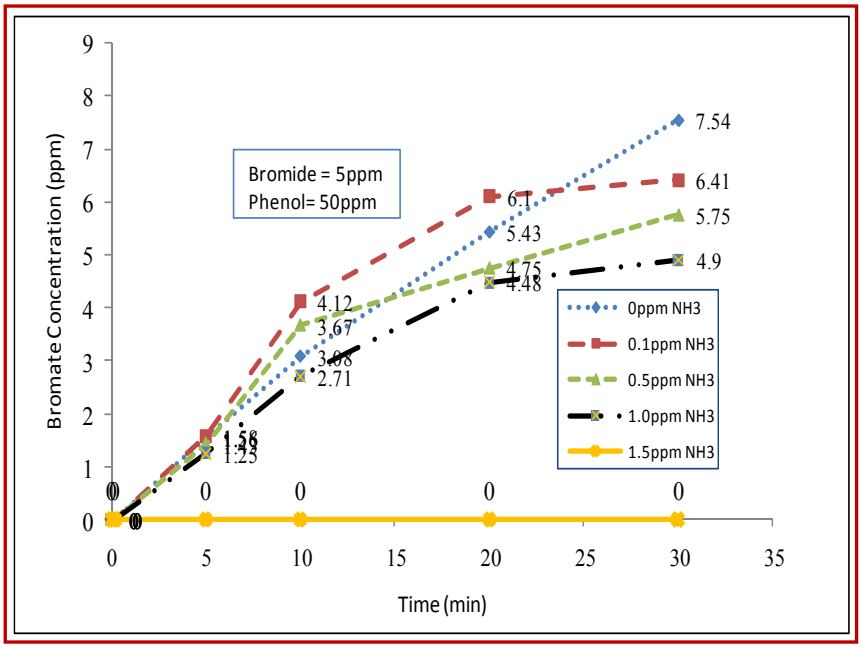

Figure 5.23: Effects of Ammonia on Bromate Minimization at pH6

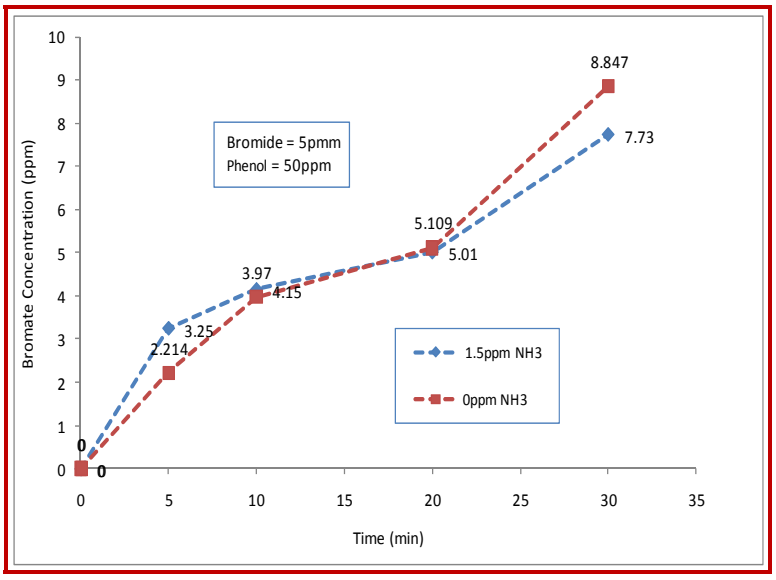

Figure 5.24: Effects of Ammonia on Bromate Minimization at pH7

5.4 VERIFICATION OF THE OPTIMIZATION AT A BASIC/ALKALINE CONDITION

After the results of several experiments conducted revealed that an additon of 1.5ppm of Ammonia is capable of completely preventing bromate formation at all pH levels lower than the ambient pH 7, this section was directed towards investigating the effects of ammonia addition at pH level higher than the ambient pH 7 i.e. basic medium. A number of experiments were conducted at pH 9, which was considered to be a suitable pH in the basic medium . All the preliminary experiments carried out on the lower pH levels were also executed at this pH before proceeding to investigating the efficieny of ammonia addition in preventing/minimizing bromate formation at this alkaline/basic pH.

5.4.1 Effects of AOP at a Basic/Alkaline pH

The study at this pH commenced by investigating the independent effects of continuous ozonation only (1 liter per minute) on the degradation of Phenol at pH 9. This experiment was necceasy to ascertain the maximum bromate concentration that could be formed at this pH level when bromate minimization strategies are not employed. Figure 5.25 shows the results of these experiments. The plot revealed that Phenol completely degraded in less than 5minutes at this pH, as observed at lower (neutral and acidic) pH levels. There was also a significant detection of bromate (8.87 ppm) after 30 minutes under this experimental condition.

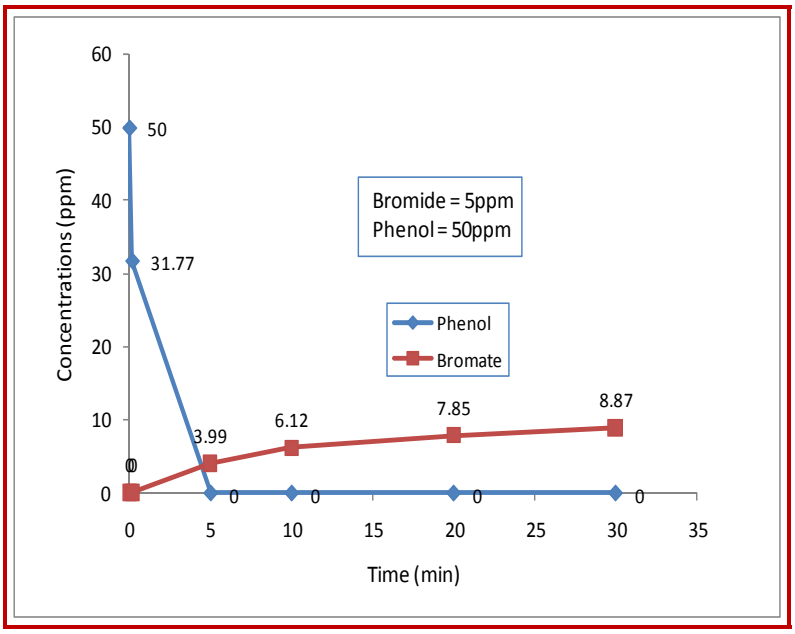

Figure 5.25: Effects of Continuous Ozonation on Phenol Degradation and Bromate Formation at a Basic pH

5.4.2 Effects of Ammonia on Bromate Minimization at a Basic pH

Having verified that continuous ozonation at pH 9, like every other pH levels, can completely degrade phenol within 5 minutes into the experiment and investigating the maximum bromate formation without an additon of ammonia, the study proceeded to explore the effects of different ammonia levels on bromate formation at this pH. Figure 5.26 summarizes the findings from all the experiments.

The Figure depicts the ability of different ammonia dosage on the inhibition of bromate formation at pH 9. Looking at the curve critically, there was no reported case of "Zero-Bromate Formation" even with the use of 1.5 ppm Ammonia concentration which completely prevented bromate formation at pH levels below pH 7 (pH 4, 5 and 6).

Figure 5.26 reveals the contribution of different ammonia concentrations (1.5 ppm, 1.0 ppm, 0.5 ppm and 0.1 ppm) in reducing bromate formation at pH 9. The figure depicts the ineffciceny of 1.5 ppm Ammonia to block the formation of bromate at this pH, a scenario similar to what was observed at pH 7. In the previous experiments conducted, an addition of 1.5 ppm Ammonia to the treated water completely blocked bromate formation at other pH levels except at pH 7. The figure also show that, ammonia was reducing the formation of bromate though, but could not prevents its formation.

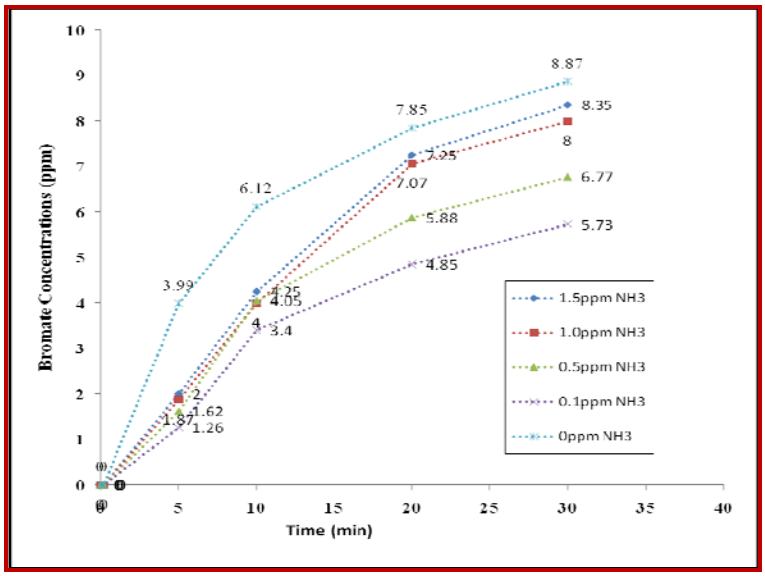

Figure 5.26: Effects of Ammonia on Bromate Formation at Basic/Alkaline pH

An addition of 1.5 ppm ammonia reduced bromate to 5.73 ppm from 8.87 ppm after 30 minutes. This is about 35% reduction in bromate level. There were also 23.6%, 9.8% and 5.9% reduction in the bromate formation with the use of 1.0 ppm, 0.5 ppm and 0.1 ppm ammonia concentrations after 30 minutes respectively. The descending trend in the effeciency of ammonia in reducing bromate formation as the ammonia levels reduces indicates that only higher ammonia concentrations are capable of blocking/preventing the oxidation of bromide to bromate.

The result obtained from pH 9 gave an inkling that the use of ammonia at inhibiting bromate formation is only effective at any pH lower than pH 7 (neutral pH), since the application of high ammonia dosage proved to be inefficient at neutral and higher pH levels (pH 7 and pH 9). This corresponds with the findings of Hoffmann and

Andrews (2006), where they also confirmed ammonia addition is insignificant at inhibiting bromate formation at higher pH values due to the fast O_3/BrO^- reaction.

CHAPTER 6

SUMMARY AND CONCLUSION

The main objective of this study was to investigate the efficiency of pH supression and ammonia addition in controlling bromate formation via ozone-based AOP. To achieve this, the research had to study the extent of bromate formation under different AOP treatment conditions (UV light, ozone dosage and contact time), study the efficiency of bromate minimization strategies (Ammonia addition and pH suppression), and finally identify the optimum conditions to inhibit the formation of bromate in water.

Results collated from several ozone-based AOP techniques evaluated, revealed that continuous ozonation at the rate of one liter per minute is faster and more efficient in degrading phenol within 5 minutes as opposed to the use of batch ozonation and the Ozone/UV methods. The batch ozonation method was not only found to be pH-dependent, but also gave incomplete removal of phenol after 30 minutes. Also, batch ozonation is not practicable, as the water had to be ozonated before being spiked by the contaminant(s). In reality, the contaminant is assumed to be in the water first, then

treated by ozonation. The combination of UV sources and continuous ozonation (UV/Ozone) gave similar results with the experiments conducted with continuous ozonation only. In both cases, phenol completely degraded within 5 minutes. The complete removal of phenol with the UV/Ozone method can be attributed to the efficiency of the continuous ozonation at removing phenol within the same duration when used alone. The use of Ozone/UV would amount to a waste of energy, if the remediation can be achieved with continuous ozonation only. Hence, the study concluded that continuous ozonation at the rate of 1liter per minute is the most effective and cost intensive ozone-based AOP technique for complete removal of phenol in water.

A number of experiments were also conducted to evaluate the effects of change in the pH levels on bromate formation. It was found that bromate formation reduces with decreased pH level under a condition of "no bromate control" (no ammonia addition). This entails that, the oxidation of bromide to bromate ions is faster in basic rather than acidic medium, which may not be unconnected with the fact that the hydroxyl radical expsoure reduces with increasing pH levels. Therefore, at lower pH levels, the overall oxidation capacity due to ozone exposure decreases, which inturn leads to a smaller bromate formation (Von Gunten et al, 2006). Hence, reducing the pH of the water could help in minimizing the amount of bromate to be generated.

The study also explored the effects of various ammonia concentrations on the minimization and/or prevention of bromate formation at different pH levels. It was

found that additon of ammnia is only effective in preventing bromate formation at pH levels lower than the ambient pH. An ammonia dosage of 1.5 ppm is capable of inhibiting the formation of bromate at any pH lower than pH 7 (ambient pH), while the same concnetration of ammonia could only reduce but not prevent the generation of bromate at neutral and basic pH (pH 7 and pH 9). An Evaluation of the efficiency of ammonia concentrations lower than 1.5 ppm (1.0 ppm, 0.5 ppm and 0.1 ppm) revealed that they can only reduce but not prevent bromate formation even at extremely low pH values (pH 4). The trend in their bromate reduction capacity also reduces as the ammonia dosage reduced. While Ammonia dosage lower than 1.5 ppm proved to successfully reduce bromate formation, the amount of bromate formed at all pH levels were higher than the maximum allowable limit of 10 ppb set for bromate ions in drinking water by the USEPA and EU. Hence, the reductions were insignificant.

Based on these results, the study concluded that in order to acheive the USEPA's maximum contminant level goal (MCLG) of zero for bromate in drinking water, the optimum ammonia concentration needed for complete prevention of bromate formation is 1.5ppm while the optimum pH for achieving this result is pH 6. This is because, it is easier and less expensive to supress the pH of water to pH 6 from pH 7 than other lower pH levels, which will require the use of higher concentrations of buffer to attain and inturn, higher chemical cost.

In summary, the following conclusions are reached at the end of this research:

1. Bromate formation reduces with decreased pH level.
2. Continuous ozonation at the rate of 1.0 liter per minute is the most effective ozone-based AOP treatment technique for complete removal of phenol in water.
3. The main degrdation by-products of phenol by ozone-based AOP were found to be: catechol, hydroquinone, para-benzoquinone and ortho-benzoquinone.
4. The optimum time for complete degradation of phenol in water using continuous ozonation under the set of experimental condtions is less than 5 minutes.
5. The optimum pH for the inhibition of bromate formation in a Saudi Arabian water is pH 6.
6. Ammonia dosage of 1.5ppm is the optimum concentration of ammonia needed to prevent the formation of bromate at the recommended optimum pH, during the AOP treatment of high-bromide containing Saudi Arabian groundwater.

CHAPTER 7

RECOMMENDATIONS

This chapter suggests reccomendations on the way forward and the findings that will lead to an improved scientific knowledge on the prevention of bromate formation during the treatment of contaminated waters by ozone-based AOP techniques. The main theme of this chapter is to investigate the potential side effects of the bromate minimization strategies employed in this research, and to verify the efficiency of the optimised treatment conditions on other contaminants. This will go a long way in ensuring the establishment of this new field of water treatment and subsequently lead to the production and supply of clean, safe and contaminants-free potable water.

The following are the proposed recommendations:

1. There is a need to investigate the removal of different contaminants other than Phenol with continuous ozonation method in combination with the bromate minimization strategies.
2. Other AOP techniques such as Ozone/hydrogen peroxide should be investigated as well.

3. It is imperative to conduct a detailed kinetic investigation on the fate of the added Ammonia.
4. A proper identification and quantification of the by-products formed during the ozonation is also necessary to ensure that the treated water is not left with newly generated contaminants.

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APPENDICES

APPENDIX A1

ANALYTICAL METHOD FOR THE ANALYSIS OF BROMATE IN WATER

Method

The method used for bromate analysis was the US Environmental Protection Agency (US EPA) method 300.1 which is commonly used for the quantification of bromate ions. A Dionex ICS 3000 Ion Chromatography (IC) with Analytical Column AS9 HC with a 9mM Na_2CO_3 eluent at a flow rate of 1.0mL/min was used in all bromate analytical runs. The IC was equipped with a Conductivity Detector (IC-CD).

1,000ppm stock bromate solution was prepared by dissolving 0.766g of potassium bromate AnalaR BDH chemical Ltd, Poole England in one Littre volumetric flask containing deionized water.

For low bromate concentration calibration, the stock solution was serially diluted to make 5, 10, 20 and 50ppb standards while 1, 2, 4, 10, 20 and 40ppm standards were prepared for high concentration bromate calibration.

Figure A1.1 and A2.2 shows the calibration curves for the low and high concentration bromate calibrations.

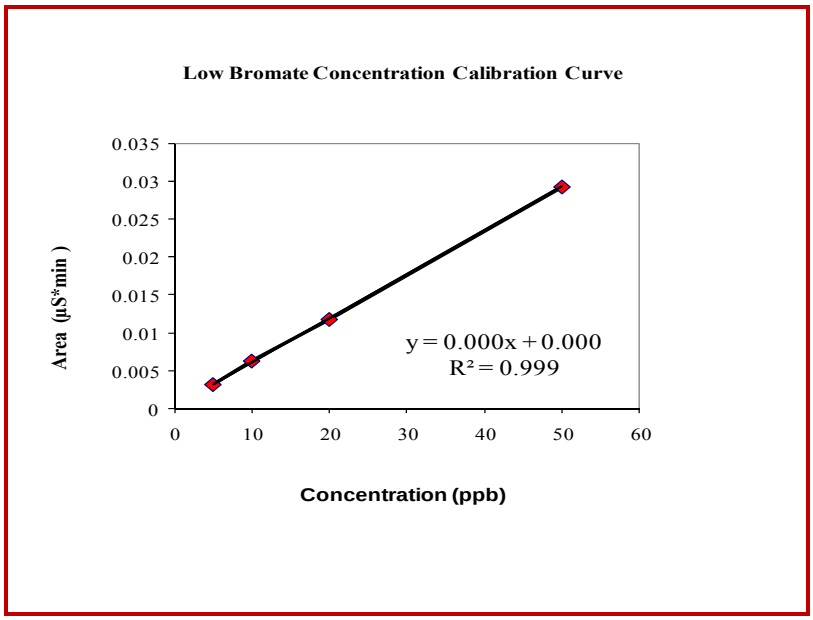


Figure A1.1 Low Bromate Concentration Calibration Curve

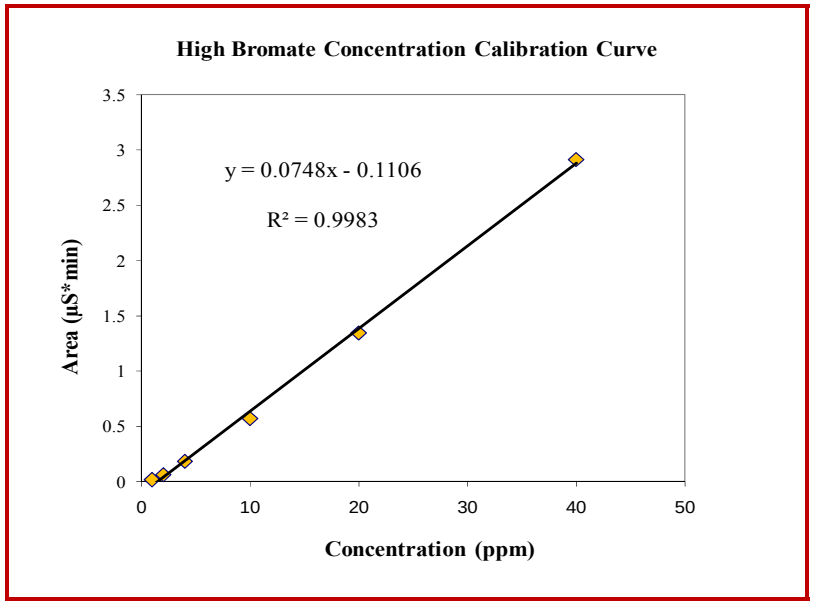


Figure A1.2: High Bromate Concentration Calibration Curve

APPENDIX A2

ANALYTICAL METHOD FOR THE ANALYSIS OF PHENOL IN WATER

Method

The concentrations of phenol were determined using the WATERS BINARY HPLC SYSTEM 1525 model equipped with the EMPOWER software, Waters Photodiode Array Detector 2996, and Waters 717-Plus Auto sampler. The system has a C-18 reverse phase column and an isocratic method with a solvent mixture of methanol-water ratio (40:60) as a mobile phase with the flow rate of 1mL/min.

5,000ppm Phenol stock solution was prepared by dissolving 5.00g of phenol crystals (99% purity) J.T Baker, U.S.A in 100mL volumetric flask containing deionized water. The stock solution was diluted serially to make 0, 10, 25 and 50ppm standards. Figure A2 shows the calibration curve for the phenol analysis.

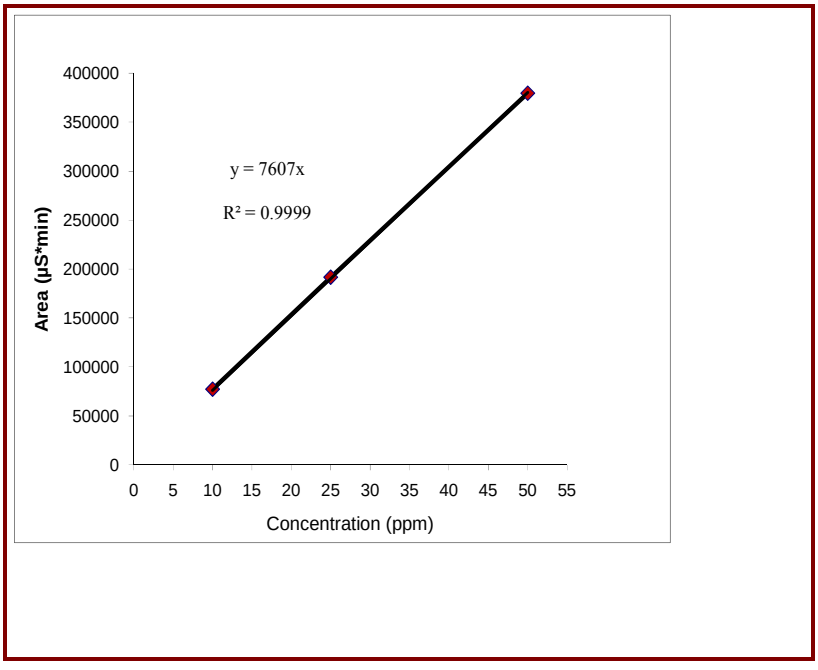


Figure A2: Phenol Calibration Curve

APPENDIX B1

CALIBRATION OF OZONE

Method:

The widely applauded Indigo method (Bader and Hoigne, 1981) for the determination of ozone in water was employed in this study.

The chemicals used for these experiments were Indigo Trisulfonate dye (BDH Chemicals Ltd, London), Orthophosphoric Acid (BDH Chemicals Ltd, London) and Sodium Dihydrogen Phosphate (Buchs Ltd). 0.6g of Indigo dye was dissolved in a 100mL volumetric flask containing deionized water, while a Phosphate buffer was prepared by dissolving 3.125g of Sodium Dihydrogen Phosphate ($NaH_2PO_4\,H_2O$) and 3.5g of Orthophosphoric Acid (H_3PO_4) in a 100mL volumetric flask containing deionized water.

The experiment commenced with the calibration of the Aquamate UV Spectrophotometer AQA2000E for the measurement ozone. To achieve this, an aqueous stock solution of ozone was first prepared by continuously bubbling ozonated oxygen (about 4%) through a gas washing bottle into distilled water chilled to 2^oC. This stock solution generally contained a steady state concentration of ozone of 40mg/L.

Standards of 0, 2, 4and 10mL aqueous ozone were prepared form the stock solution as shown in the table B1.

Table B1: preparation of Standards for ozone measurement

Volume of Ozone Stock (mL)	Concentration of the Standard (ppm)	Phosphate Buffer (mL)	Indigo Solution (mL)
0	0	10	4
5	2	10	4
10	4	10	4
25	10	10	4

The standards were calibrated by measuring their absorbance at 258nm on the Aquamate Spectrophotometer and the calibration curve generated is shown in figure B1 below:

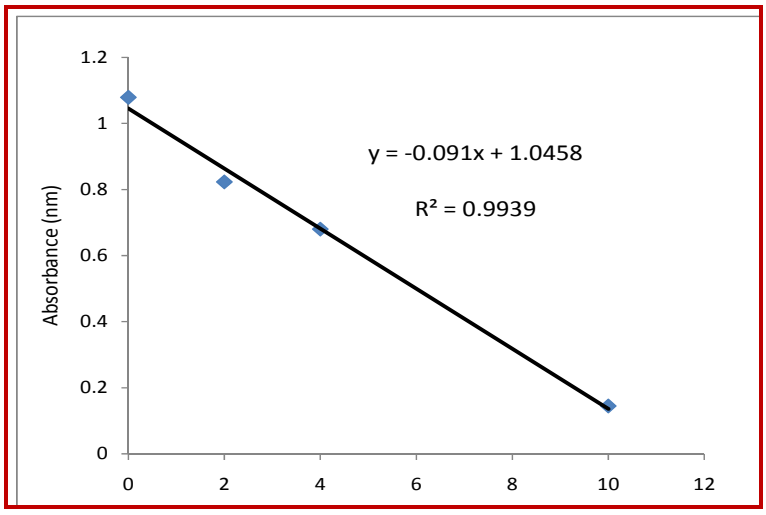


Figure B1: Ozone Calibration Curve

APPENDIX B2

OZONE MEASUREMENT

Method: To quantify the concentration of ozone dissolved in water using the Indigo method of Baider and Hoigne (1981), the following procedures were followed:

1. The reactor was filled with 450mL buffered water (pH 4.0).
2. The temperature of the water was kept at room temperature.
3. Ozone generator was turned on to supply ozone at a controlled rate of 1.0 liters per minute.
4. Samples were taken at time 0, 5, 10, 15, 20, 30 and 40 minutes respectively into 10mL volumetric flasks containing 4mL indigo dye solution and 10mL phosphate buffer solution.
5. The samples were preserved with sodium thiosulphite.
6. The samples collected were analyzed on the Aquamate Spectrophotometer using the already generated ozone calibration equation.

Table B2 shows the results obtained:

Table B2: Ozone Measurement

Time (min)	Concentration (ppm)
0	0.0
5	5.0
10	6.6
15	8.5
20	10.0
30	10.0
40	10.0

APPENDIX C

BUFFER RECIPES’

Buffer Recipe for pH 4.0

According to the recipe, 0.1 Molar of KH_2PO_4 when dissolved in 100mL volumetric flask will give a Buffer of pH 4.0.

KH_2PO_4, Fluka A.G, HPLC grade, Buchs Ltd was used in the preparation of the stock buffer solution.

The following calculations were made to determine the quantity of KH_2PO_4 needed to prepare 0.1 Molar of the reagent in a 100mL.

Molarity = Moles/Liter

0.1M = Moles/Liter

Moles = 0.1M x Liter

Mole = Weight in grams/Molecular weight

The molecular weight of KH_2PO_4 = 136.09g/mole

Weight in grams = Mole x Molecular weight

Weight in grams = 0.1 x 136.09

Weight in grams = 13.609g/Liter.

To prepare 13.609g of KH_2PO_4 in a 2 Liter container; 13.609g x 2 = 27.218g

Hence, 27.218g of KH_2PO_4 was weighed and dissolved in a 2000mL volumetric flask containing deionized water and stored in a clean container as a stock buffered water of pH 4.0.

Buffer Recipe for pH 5.0

27.218g of KH_2PO_4 (0.1Molar) Fluka A.G, HPLC grade, Buchs Ltd was weighed and dissolved in a 2000mL volumetric flask containing deionized water. The pH of the water was checked using the pH meter and the pH was found to be 4.0.

0.1Molar of NaOH solution was prepared by weighing 0.4g of NaOH pellets Fluka A.G, Switzerland, in a 100mL volumetric flask of deionized water.

20mL of the prepared 0.1Molar NaOH solution was successively spiked into the volumetric flask containing KH_2PO_4 solution through an eppendorf. The pH of the buffer was carefully monitored with the pH meter until the pH became 5.0.

Buffer Recipe for pH 6.0

27.218g of KH_2PO_4 (0.1Molar) Fluka A.G, HPLC grade, Buchs Ltd was weighed and dissolved in a 2000mL volumetric flask containing deionized water. The pH of the water was checked using the pH meter and the pH was found to be 4.0.

0.1Molar of NaOH solution was prepared by weighing 0.4g of NaOH pellets Fluka A.G, Switzerland, in a 100mL volumetric flask of deionized water.

172mL of the prepared 0.1Molar NaOH solution was successively spiked into the volumetric flask containing KH_2PO_4 solution through an eppendorf. The pH of the buffer was carefully monitored with the pH meter until the pH became 6.0.

Buffer Recipe for pH 7.0

2.70218g of KH_2PO_4 (0.01Molar) Fluka A.G, HPLC grade, Buchs Ltd was weighed and dissolved in a 2000mL volumetric flask containing deionized water.

0.1Molar of NaOH solution was prepared by weighing 0.4g of NaOH pellets Fluka A.G, Switzerland, in a 100mL volumetric flask of deionized water.

65mL of the prepared 0.1Molar NaOH solution was successively spiked into the volumetric flask containing KH_2PO_4 solution through a 50µL eppendorf. The pH of the buffer was carefully monitored with the pH meter until the pH became 7.0.

Buffer Recipe for pH 9.0

0.05Molar of $NaHCO_3$ E.Merck Chemicals Ltd was used in preparing the buffered water at pH 9.0

The volume of $NaHCO_3$ required to give 0.05Molar was calculated as thus:

Molarity = Moles/Liter

Mole = Weight in grams/Molecular weight

The Molecular weight of $NaHCO_3$ is 84g/mole

Weight in grams = Moles x Molecular weight

Weight in grams = 84g/mole x 0.05Molar

Weight in grams = 4.2g/Liter.

In a two liters volumetric flask: 4.2g/Liter x 2 = 8.4g/Liter

Hence, 8.4g of $NaHCO_3$ was weighed and dissolved in a 2000mL volumetric flask of distilled water.

APPENDIX D

IC CHROMATOGRAMS

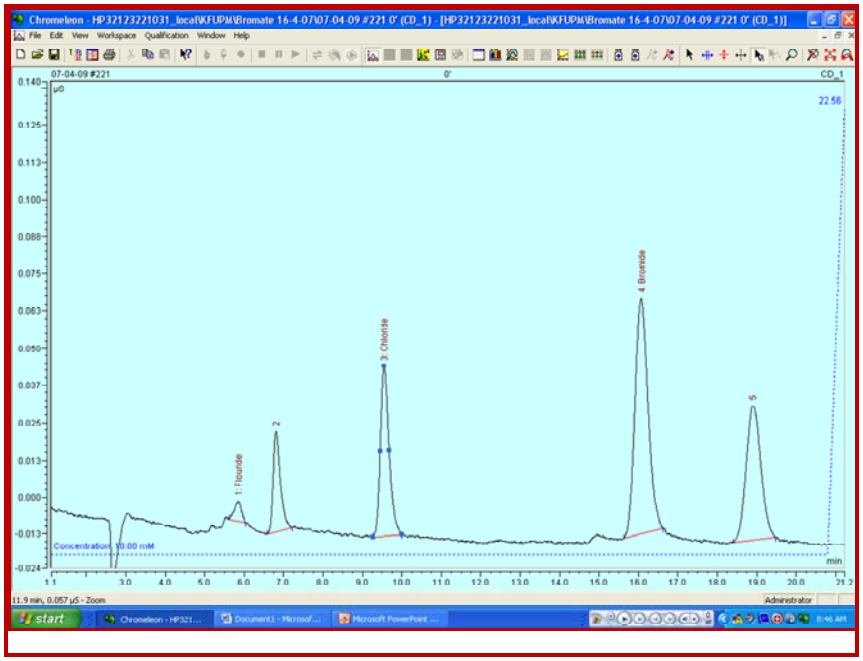


Figure D1: IC Chromatogram at time t = 0minute

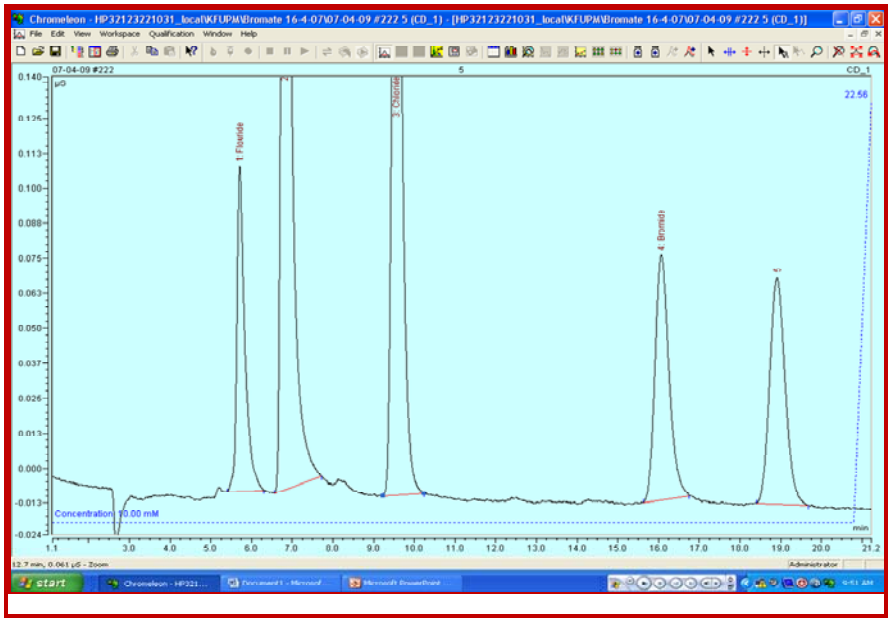


Figure D2: IC Chromatogram at time t = 5minutes

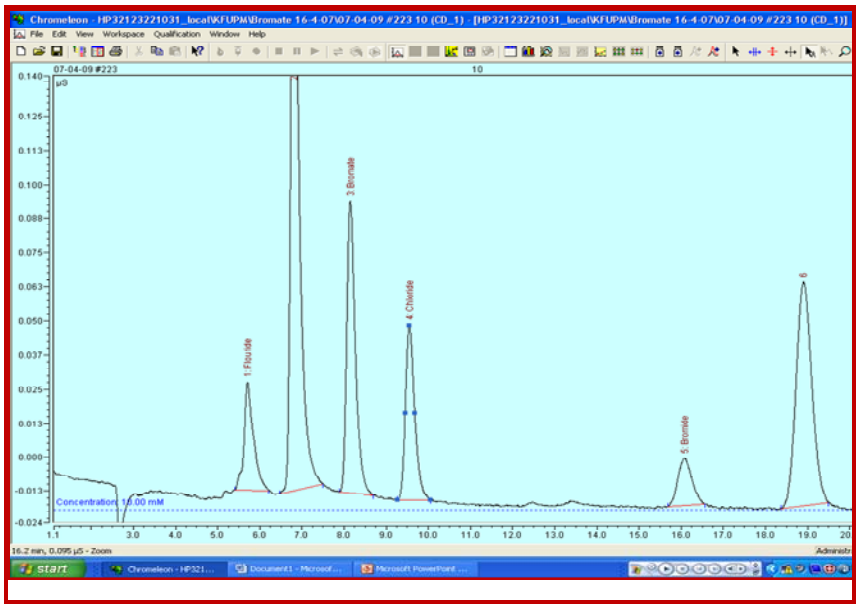


Figure D3: IC Chromatogram at time t = 10minutes

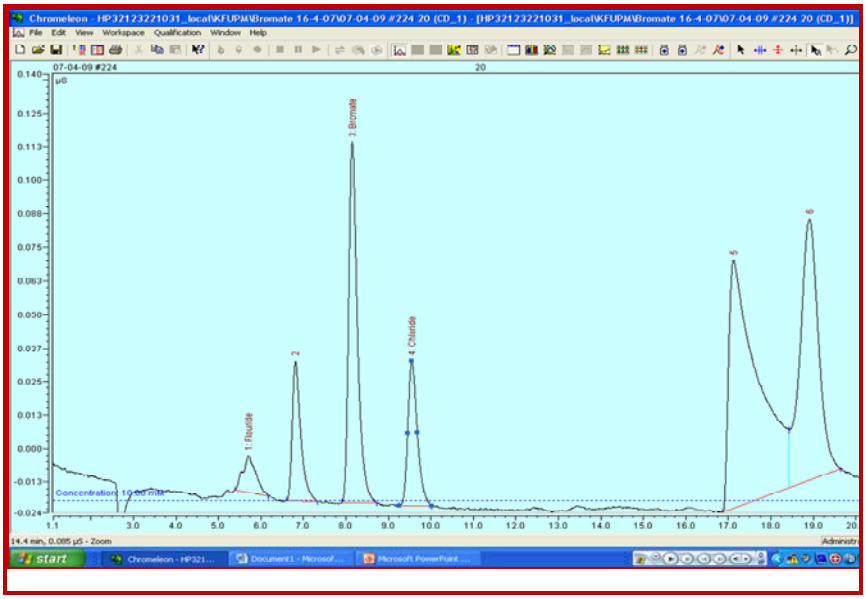


Figure D4: IC Chromatogram at time t = 20minutes

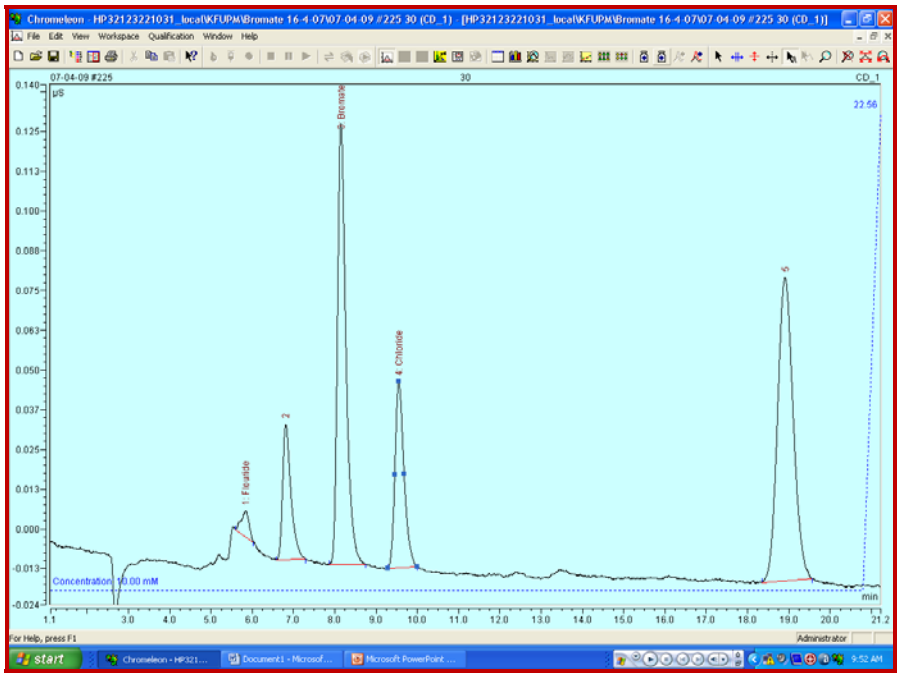
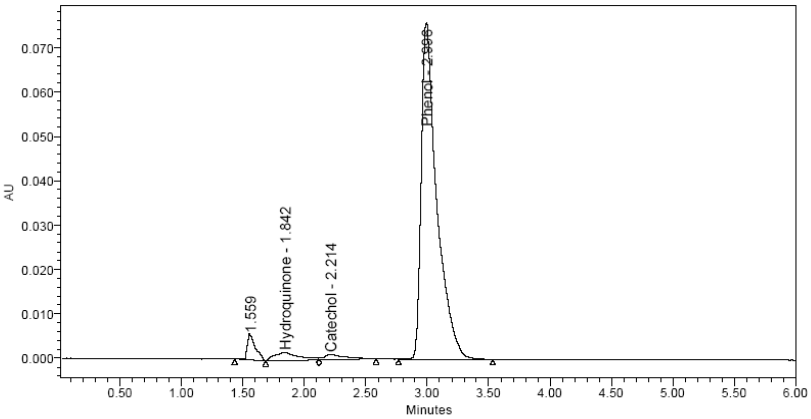


Figure D5: IC Chromatogram at time t = 30minutes

APPENDIX E

HPLC CHROMATOGRAM



	Peak Name	RT	Area	% Area	Height	Amount	Units
1	Benzoquinone	1.281					
2		1.559	26535	3.63	5601		
3	Hydroquinone	1.842	24829	3.40	1801	1.751	ppm
4	Catechol	2.214	13425	1.84	1205	0.162	ppm
5	Phenol	2.996	666034	91.13	75811	6.776	ppm

HPLC Chromatogram showing phenol and other by-products

APPENDIX F

EXPERIMENTAL PLAN

VITA

Abdulrazaq Zubair was born in Nigeria. He received his B.Sc in Soil Sciences from University of Maiduguri, Nigeria in 2005. He worked as a Research Officer with Rubber Research Institute of Nigeria (RRIN) between September 2006 and August 2007. He joined the Environmental Sciences program of the Earth Sciences Department at King Fahd University of Petroleum and Minerals (KFUPM) in August 2007 as a Research Assistant and completed his Master of Science (MSc) in June 2009.

His research interests include Soil and Water Remediation, Environmental Impacts Assessment and Waste Management.

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